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EDITORIAL

Industrial Conditions

ACCURATE information about industrial conditions is often very late in appearing for it involves a careful examination of a huge mass of statistics that have taken a long time to collect. The Census of Production in the Industrial Areas of Great Britain for the year 1930 is now approaching completion and the leading results of it appear in *The Times Trade and Engineering Supplement* for March 11. It appears that the gross output of the ten great industrial areas of Great Britain declined from £3,427,000 in 1924 to £2,978,000 in 1930: that the net output per man has remained almost the same and that the mechanical power ordinarily in use has increased from 16,929,000 h.p. in 1924 to 22,135,000 h.p. in 1930. The figures we published in our issue of March 3 show that our present industrial output is now about ten per cent less than it was in 1930 so that we can judge of the decline in production and be thankful that its rapid drop is at an end so far as this country is concerned. There are many causes for the present troubled state of the world and we do not propose to enumerate them; possibly there are as many remedies as there are causes although some of our optimistic friends think that one simple remedy such as inflation, or free-trade, or communism will be a universal panacea. Two factors that are sometimes forgotten have been again called to our attention by articles in the *Lancet* for March 4. The first is the change taking place in the quantity and quality of the human population. There is a possibility, if not a probability, that the populations of Germany, France, Great Britain, and the United States may diminish instead of expanding. This will mean a decreased demand for foodstuffs and sundry raw materials and, unless great changes take place in our social conditions, for many manufactured articles. The second factor is illustrated by an account of the removal of a slum population to modern dwellings in Stockton-on-Tees. An unhealthy area in that borough was pulled down in 1927 and the inhabitants were housed in a new self-contained municipal housing estate. The old slums were insanitary and bad; the new estate offered everything that modern sanitary science could demand. To the surprise of all concerned the death-rate for the new estate was higher than that of the old slums and it increased until it became necessary to make a special investigation. The only fact that seemed to offer an explanation was that the rent in the new estate came to about 8s. 10d. per family per week and the rent in the old slum was about 4s. 10d. per family per week. This additional expenditure on rent compelled the families to cut down their expenditure on food until their health was very seriously affected. This same sort of cause is operating in other boroughs besides Stockton-on-Tees; rents are tending to become higher and higher as the capital cost of building increases and if this continues to operate the purchasing power of a large proportion of the population will decline instead of increase.

British Pharmacopœia in Australia

The Drug Houses of Australia, Ltd. have published a very convenient guide to the new British Pharmacopœia which calls attention to the important changes in that time-honoured publication. These changes are now known to every pharmacist and druggist in this country and we shall not mention any of them in detail; those who are concerned in the dispensing of drugs do not require an editor's comments on them. The British Pharmacopœia was first published in 1854 and the D.H.A. Guide to the present B.P. considers that the last issue is not only better than its predecessors but is far in advance of any of the most recent pharmacopœias. The Drug Houses of Australia, Ltd. call attention to the practice of issuing advance copies of the B.P. in London and some other cities in these islands for three months prior to the issue of the pharmacopœia itself and they consider it somewhat anomalous that other parts of the Empire were not similarly favoured so far as conditions of time and space rendered this possible. We hesitate to be dogmatic on such a matter as this, but if the new B.P. is as excellent as we believe it to be, and if it is likely to be used in places far over the seas, surely no harm would be done and no very great expense incurred by the dissemination of a few extra copies to our Dominions.

CORROSION OF METALS IN SALT SOLUTIONS AND SEAWATER

JUBILEE MEMORIAL LECTURE, 1932-33

By Dr. G. D. BENGOUGH

(Concluded from page 210)

The explanation of the low post-parabolic slope may be that in N/10 some anodically formed corrosion product such as ferrous hydroxide quickly checks the high initial corrosion rate; owing to the pervious nature of the magnetic and ferric oxides formed in this solution some negatively charged hydroxyl ions will drift to the anode and assist in the maintenance of the ferrous film. In the dilute solutions an impermeable barrier of hard corrosion product is soon built up between the attacked and unattacked areas and may prevent hydroxyl ions reaching the anode; consequently there is less chance of a permanent film being maintained there, and corrosion can continue at its initial rate till the "mounds" cut it down. Increased oxygen supply will not much increase corrosion, however, owing to the limited supply of Cl ions at the anode.

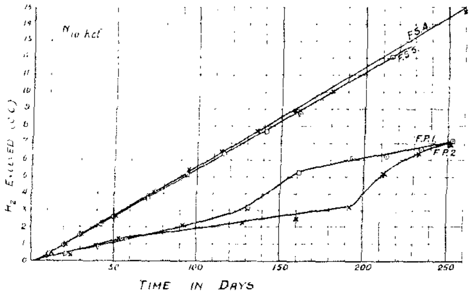


Fig. 23

Hydrogen curves. N/10 KCl. F.S. 4 and 5 mild steel. F.P. 1 and 2 pure iron

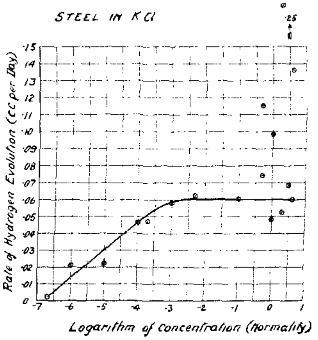


Fig. 24

Hydrogen rate-log conc. KCl

Hydrogen gas was evolved in all experiments with both purified iron and steel in all the solutions used. Part of this gas may result from a reaction between ferrous hydroxide and water, as suggested by Schikorr, but most of it probably results from reaction with the metal. In weak solutions the hydrogen time curves are similar in form to the corresponding corrosion time curves except with pure iron which gives linear curves. In N/10 KCl and stronger solutions the curves are approximately straight lines through the origin; but with pure iron abrupt changes of slope sometimes occur (see Fig. 23). There was no induction period as with zinc, and much less hydrogen was evolved from purified iron than from steel in similar conditions.

The effect of KCl concentration is shown in Fig. 24. Two outstanding facts have been discovered:

(1) In spite of sudden irregularities there seems to be a common rate of gas evolution from all solutions stronger than N/1000 although both the corrosion rate corresponding to the oxygen absorption process, and the oxygen solubility are falling. These results are similar to those found for zinc, with which the final steady rate was the same for all solutions stronger than N/10. This suggests that the hydrogen gas process is independent of the oxygen absorption process and of oxygen solubility over the range considered. It may be further suggested that the hydrogen gas is not simply an excess which escapes oxidation, but that its rate of evolution is mainly determined by some other factor than oxygen supply. Specimens in solutions of N/2 KCl and stronger usually show the hydrogen evolution rate of 0·06 c.c. per day, but some show a considerably higher rate. The reasons for the great variations in rates in this range are not known.

(2) There is a similarity between the hydrogen/time curves and the corrosion/time curves for the weak solutions. A straight line curve is obtained if the values for the total hydrogen evolutions are plotted against the corresponding values for the total oxygen absorbed. This suggests that a similar factor is at work controlling the corrosion corresponding to both sets of curves. Since hydrogen evolution appears to be independent of oxygen variations, it seems possible that anodic polarization is playing an important part in determining the corrosion in these solutions, as already suggested for other reasons.

The proportions of the total corrosion in various solutions that are due to hydrogen evolution are shown in Table VIII.

Corrosion in sodium chloride and natural seawater.—Seawater is often assumed to correspond roughly to a solution N/2 NaCl, but it has been found that there are differences of surprising magnitude between the rates of corrosion in KCl and NaCl of similar concentration, far greater than can be accounted for by differences of oxygen solubility. Curves for N/2 solutions are given in Fig. 25.

Though N/2 NaCl corresponds approximately to the

concentration of salt in seawater, yet the corrosion/time curves for steel in the two solutions are widely different, as shown in Fig. 26. With restricted oxygen supplies, such as characterized our standard experiments, the

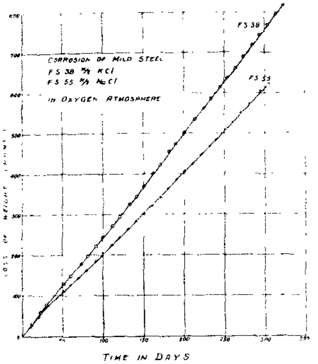


FIG. 25

Corrosion/time curves in N/2 KCl and N/2 NaCl

corrosion rate is faster in seawater than in N/2 NaCl; hydrogen evolution especially is much greater, and contributes a large proportion of the total, a fact that has been generally overlooked till quite recently. The *cause of the high rate of evolution in seawater is connected with the presence of some organic constituent that has not yet been identified.* With higher rates of oxygen supply the absolute rate of hydrogen evolution is not much altered; consequently, the proportion due to it falls (see Table VIII). Moreover, the greater

TABLE VIII

Mild steel in standard conditions

Corrosion at end of 100 days (mg.)

Oxygen atmosphere		I By H evolution	II By O absorption	Total corrosion. I + II	% due to H
Totally immersed	N/2 NaCl	11	192	203	5·6
	Seawater	90	165	255	35
Partially immersed	N/2 NaCl	10	1183	1193	0·85
	Seawater	84	720	804	10·5
Air					
Totally immersed	N/2 NaCl	23	62	·85	27
	Seawater	116	66	182	64
	N/10 KCl	16	72	88	18

oxygen supply does not increase the corrosion in seawater so much as in the salt solution; consequently the corrosion rate in the latter becomes greater than in seawater, with high rates of oxygen supply. The lower response of the corrosion rate in seawater to increase of oxygen supply may possibly be due to the presence of a film of magnesium compounds, but the matter has not yet been fully cleared up.

The apparatus in which all the foregoing work has been done has important limitations in practice: (1) It is expensive. (2) It cannot easily be used with atmospheric air without change of composition. (3) Corrosion rates are rather slow, though, when oxygen is used, not so slow as in open beakers. I shall now discuss our attempts to meet one or other of these drawbacks.

In the standard thermostated apparatus the oxygen is supplied to the metal partly by diffusion and partly by mild convection currents set up by the corrosion process itself. Stronger convection currents may be set up by immersing only the bottom half of a standard apparatus in a thermostat or by simply placing it on a bench. The extra currents will cause faster, but *variable*, corrosion rates. If the laboratory temperatures are reasonably constant a mean corrosion-time curve can be drawn through the points obtained by averaging the readings over, say, 10-day periods. The curve is still approximately linear but the slope is increased and liable to abrupt changes; reproducibility is considerably lowered. Table IX gives the *order* of rate that can be reached in various conditions during the first year of corrosion. If it be desired to increase the rate of corrosion still further, vessels of larger cross section can be used (see Fig. 5). For some purposes this is highly important because the relative corrosion rates of the same material in two different solutions *may be altered, or even reversed in order, if the rate of oxygen supply is altered, as in the important case of sodium chloride solutions and seawater, as will be* seen from Table IX.

A much simpler type of apparatus, based on loss of weight measurements, can be used if it is not necessary to discriminate between hydrogen and oxygen corrosion —for instance, when a preliminary investigation has established their relative amounts. An appropriate apparatus is shown in Fig. 27. It possesses the advantage that its atmosphere can be swept out and renewed at frequent intervals so that the concentration of any constituent present in small amount, such as CO_2 in air, can be kept up; this cannot be done conveniently

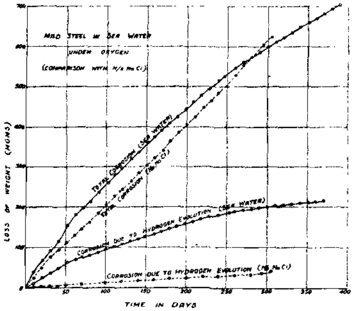


FIG. 26

Corrosion/time curves for seawater and N/2 NaCl

with the more elaborate apparatus which is normally used with either oxygen or "purified air." Comparison between results obtained in the two types has shown, however, that the effect of the CO_2 in the air is small as

regards the total amount of corrosion of mild steel, except in weak solutions and, possibly, in very long experiments. An apparatus developed at Teddington for getting high rates of corrosion by means of increased oxygen pressures is shown in Fig. 28. It is an adaptation of the simple vessel, but gives results in duplicate. The total amount of hydrogen evolved can be obtained at the end of an experiment by pumping out the gas and analysing it, but hydrogen-time curves are not easy to get.

TABLE IX

Standard specimens of mild steel

Corrosion rates in mg. per day

N/10 potassium chloride

Experimental conditions	Atmosphere	Diam. of vessel, cm.	Immersion depth, cm.	Mg. per day
Thermostated 25°	*Oxygen*	4·4	0·035	21·5
,,	,,	15·0	1·5	11·0
"Half thermostated"	,,	4·4	1·5	7·7
Thermostated 25°	,,	4·4	1·5	2·75
,,	Air	4·4	1·5	0·73

N/2 sodium chloride and seawater

Experimental conditions	Atmosphere	Diam. of vessel, cm.	Immersion depth, cm.	NaCl	Seawater
Thermostated 25°	Oxygen	15·0	1·5	8·7	5·5
Laboratory temps.	Air	30 (sq.)	1·5	2·9	2·2 (1·85)
,, ,,	,,	25·4	1·5	2·7	2·5
Regulated convection	Oxygen	4·4	1·5	2·3	—
Thermostated 25°	,,	4·4	1·5	1·84	1·95
,,	Air	4·4	1·5	0·66	1·33

All measurements are taken from the most persistent linear slopes of corrosion/time curves.

The average rate of corrosion in Friend's seawater tests at Halifax and Auckland, for comparable size of specimens, would have been about 3·75 mg. per day; in Southampton dock about 1·6, and at Weston about 3·80 (calculated for a five-year period.)

Experiments in large open vessels were made in order to investigate the relative rates of corrosion of mild steel in N/2 NaCl and seawater in presence of ordinary convection currents. Table IX shows that in our standard thermostated conditions the corrosion rate in seawater and air is faster than that in N/2 NaCl, and this is also true if oxygen be substituted or if a corrosion vessel 15 cm. in diameter be used with air. But if oxygen be used in the larger vessel, or if a 30-cm. square vessel be used and exposed to fluctuations of laboratory conditions so that Adeney convection currents occur, the corrosion is greater in N/2 NaCl. In Friend's field tests at Halifax and Auckland the maximum loss of weight divided by the total time of test gives a result of about 0·25 mg. per sq. cm. per day or about 3·75 mg. for specimens of our size. This is exceeded in our conditions with seawater only by the use of oxygen and a large vessel.

The inversion of the rates of corrosion in seawater and N/2 NaCl shows that the effect of Adeney convection currents may become important even in apparently stagnant conditions. Consequently some curves were obtained in unthermostated, but otherwise standard, conditions. Those shown in Fig. 29 are for specimens in N/10 KCl exposed to the air under a glazed wooden cover which merely excluded draughts. Losses of weight were determined for duplicates at the end of fixed times and agreed fairly well. Moderately good curves could be plotted, however, in spite of erratic temperature changes which would affect each pair of duplicates alike, but different pairs to different extents according to whether or not they had been withdrawn from the test when the changes occurred. The average slope of the curve is 1·76 mg. per day, *i.e.*, about 2½ times the standard rate (0·73) in air, but less than in oxygen (2·75). Reproducibility of such curves is low.

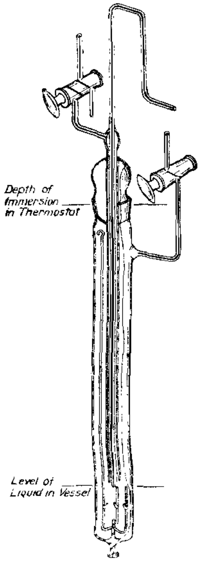


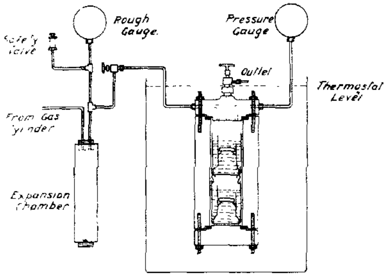
FIG. 27

Simple corrosion apparatus

Summing up, we have found that in the absence of ordinary and Adeney convection currents we can get good reproducibility, but high corrosion rates should be used with the help of oxygen or large vessels or increased pressures. In the presence of convection currents reproducibility is poor but the results represent ordinary conditions of immersion in apparently stagnant conditions. A useful line of work which suggests itself is to devise a method which would give controlled and approximately constant convection currents of similar average strength to those that occur in typical stagnant immersed conditions in the atmosphere.

An apparatus designed for the purpose is now being tested. The idea is to produce a constant convection

current by maintaining the bottom of a brass container in which the corrosion vessels are placed at a constant temperature of 25° C. by immersion in a thermostat, but its top at a different temperature by keeping it above the water level. Preferably the thermostat should be



By permission of the Faraday Society

FIG. 28

High-pressure apparatus

placed in a room kept constant at a lower temperature than 25° C. Since no such room was available a preliminary test was made by using a draught shield placed over the top of the brass container which was thereby exposed to temperatures which fluctuated between the limits 29° and 23·6 during July and August. Corrosion rate in N/2 NaCl were about 2·3 mg per day (standard rate 1·84). A curve obtained in this apparatus is shown

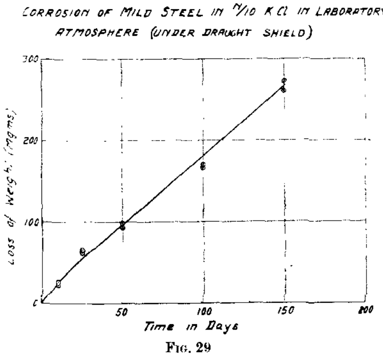


FIG. 29

in Fig. 30; it is better than expected, but improved methods are now being tried.

With convection currents of this type corrosion is still slow and experiments should be carried on for a year or two if adequate knowledge of corrosion rates is to be obtained. This raises the question of an "accelerated test." Our definition of this is as follows: "an accelerated corrosion test is one which reproduces the corrosion-time curve characteristic of any given metal in standard conditions, with the time-scale suitably expanded." It must be based on a knowledge of the factor which controls the corrosion rate in the arbitrarily selected standard conditions.

Fig. 31 shows a simple example of such a test in thermostated conditions in which the time scale is multiplied 3·6 times. It was based on the knowledge that the rate of oxygen supply controlled the rate of corrosion, and this rate was increased by merely increasing the cross section of the vessel about 11 times. Further increases, however, would be useless; in fact, a maximum effect is reached with an increase of cross section of about 5 times. The most effective method of ensuring still greater oxygen supplies in stagnant conditions is by the use of high pressures, and it might be thought possible to arrive at a "maximum acceleration test" at some high oxygen pressure, just above which some new factor would begin to control the corrosion process.

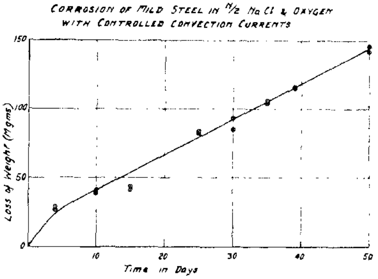


FIG. 30

Unfortunately the matter is not quite so simple as this. Fig. 6 shows the influence of oxygen pressure on corrosion rates in our standard conditions. Evidently about 20 atmospheres is the highest to which we can go, since the curve becomes flattened above that pressure. But even below it we are in difficulties. The slope of the main linear part of the curve is given by the pressure multiplied by 1·76 c.c. of oxygen absorbed per day* and not by 0·84 c.c. which we saw was the long-persistent linear slope for mild steel. But you will remember that a greater slope, 1·44, was reached for a time between 400 and 500 days. Increased pressure, therefore, gives a higher rate than would be expected even from this rate. Why should this be? Suggestions only, and not a definite answer, can be made at present.

Fig. 6 shows that the first 2 or 3 atmospheres increase corrosion less than subsequent increases; this is probably due to oxygen being used up for the rapid oxidation and destruction of the obstructive film of ferrous hydroxide which dictated the low (0·84) slope: when this is once

* The equation of the linear part of the curve is $O = 6{\cdot}5 + 1{\cdot}76(P-5)$, where O is the oxygen absorption rate, P the pressure in atmospheres, 6·5 the rate of absorption at 5 atmospheres.

destroyed the corrosion rate may increase proportionately to the pressure and we get a linear pressure/corrosion curve. At pressures up to one atmosphere of oxygen this obstructive film is, perhaps, partially destroyed after lapse of a long time, possibly by the roughening of the metal which undercuts the film. With high oxygen pressures the film may be destroyed much sooner, or perhaps never formed; if so, we have altered one of the factors in our attempted acceleration test, which must therefore be interpreted with circumspection. Nevertheless, the matter is worth further investigation, particularly because in this type of test ordinary air can be used, and the residue replaced periodically so as to maintain composition.

Now as to the way in which the results of corrosion measurements are often stated. A practice, originated and widely used in America, is creeping into this country but should, in my opinion, be absolutely abandoned. It consists in stating results of the loss of weight type, obtained for short and arbitrarily chosen times, as rates of penetration *per year*, apparently on the assumption that the distribution will not alter with time and that the corrosion/time curves are linear for at least 365 days. In an extreme case the results of four-day experiments have been so treated. Yet few laboratory experiments described in the literature have been carried on for a year and still fewer penetration measurements and corrosion/time curves have been made for that period. Most of the latter have been obtained by ourselves in "apparently stagnant" conditions; none of these consists of a straight line through the origin for a year. The practice mentioned gives a specious air of importance to short experiments which may mislead many people, especially those who read only the abstracts of papers in which experimental details cannot be given.

The Distribution of Corrosion

Corrosion/time curves give us much important information about the corrosion process, but do not tell the whole story; it is, therefore, particularly interesting to study distribution on specimens for which corrosion/time curves have already been obtained. I will first remind you of the electrochemical nature of the corrosion process in these solutions. Table X summarizes the principal reactions, ignoring the mechanism whereby metal ions first enter solution—a debatable matter. Note particularly that metallic hydroxide can be formed in at least two physically distinct varieties, one a fairly continuous film which may be protective, and the other loose and either non-protective or only slightly protective. The first is formed at cathodic areas and must be pervious to electrons, or the whole electrochemical process would cease, but nearly impervious to metal ions, which can only ooze slowly through it and are then immediately precipitated by alkali; on zinc a visible film may be gradually built up, but often only an invisible one on steel. The other variety consists largely of loose flocculent masses easily shaken off the metal; on steel these are mainly black magnetic oxide and ferric oxide of the γ variety.

Obviously these masses of corrosion product must allow metallic ions to pass freely out from the metal or corrosion would cease; it is usually assumed that they are, nevertheless, almost impervious to dissolved oxygen and so able to cause differential aëration sufficient to exert an important influence on the distribution of corrosion. I believe, however, that dissolved oxygen will not commonly be sieved out by a corrosion product which is pervious to ions; both or neither will pass through.

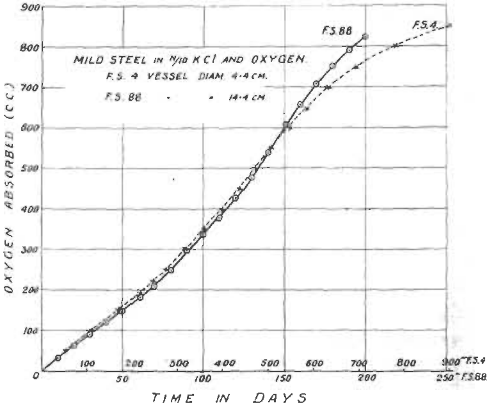


Fig. 31

Acceleration of corrosion by use of wide vessel

TABLE X

Reactions of Zn and Fe in NaCl solution

At anodes	
$2(OH)' + M^{\cdot\cdot}$	$\rightarrow M(OH)_2$ (protective or not, according to M and the conditions) $\downarrow$
$2Cl' + M^{\cdot\cdot}$	$\rightarrow MCl_2$ (soluble)
At cathodes	
$2H$	$\rightarrow H_2$ (gas)
$2H + \frac{1}{2}O_2$	$\rightarrow H_2O$
$2(OH)' + M^{\cdot\cdot}$	$\rightarrow M(OH)_2$ (protective in alkaline conditions) $\downarrow$
$2(OH)' + 2Na^{\cdot}$	$\rightarrow 2NaOH$
In body of liquid	
$2NaOH + MCl_2$	$\rightarrow M(OH)_2 + 2NaCl_2$ (often as loose masses over anodes) $\downarrow$

Note.—The table is not intended to show the *proportion* in which the different actions occur; thus the amounts of hydrogen set free as gas, and oxidized to water, may vary greatly with the conditions.

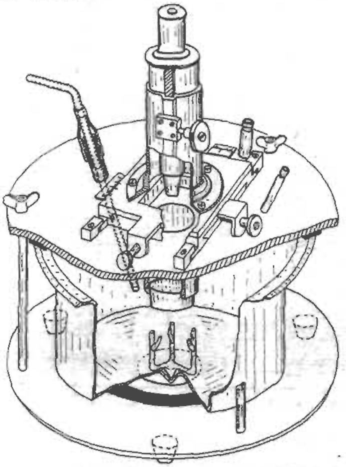


FIG. 32
Photographic apparatus

DISTRIBUTION OF CORROSION ON ZINC

The apparatus used for following and recording changes of distribution with time on a single specimen is shown diagrammatically in Fig. 32. The distribution of corrosion on zinc in conductivity water is shown in Fig. 33. It is concentrated at centres sparsely and fairly uniformly distributed over the surface of Australian electrolytic zinc in conductivity water; round each corrosion centre rings occur of white precipitated zinc hydroxide and, further out, of "interference colours," which probably also consist of corrosion product. The total corrosion is very slight and ceases entirely after a few hours, probably owing to the formation of a protective film of hydroxide. The loci of the corrosion centres are probably decided by slight physical differences in the metal, produced largely by the process of preparing the metal surface. Evans and others state that these loci correspond to "weak points" in an oxide film formed on the surface of the metal on exposure to air or oxygen and, no doubt, those atoms will be specially

FIG. 33
Zinc after 3 hours in conductivity water

ready to react which are not associated with oxygen. In salt solutions, even of moderate strength, the loci are initially very numerous so the air-formed film must be very full of holes.

Fig. 34 (Plate I) shows the distribution on a specimen of A.E. zinc in N/10,000 K_2SO_4 at the end of 27 minutes and 5 days; the loci are numerous but in half an hour have already sensibly diminished in number since the beginning of the experiment. Corrosion persists at some of them, but the corrosion rate in this solution steadily diminishes in a similar manner to that in Fig. 35. This has been shown to be due to a general increase of alkali in the solution; it is, therefore, reasonable to suppose that the suppression of many of the centres is due to the spreading of alkali over them—particularly since alkali is known to cling tenaciously to, and spread over, metal surfaces and to damp down the corrosion of

FIG. 33A
Zinc in "equilibrium" water $4\frac{1}{2}$ hrs. (× 2)

zinc, when present in moderate concentration, by causing the formation of a protective hydroxide film.

This suppression of less active, and persistence of, and spreading from, more active centres results in a secondary distribution, which is illustrated in more

detail in Fig. 36 (Plate I). It soon results in the building up of walls of corrosion product which divide the attacked from the relatively unattacked areas; beneath the walls themselves there is no attack.

In dilute solutions spreading from reactive centres can never proceed very far, since the whole process soon stops, even in fairly large laboratory vessels. In stronger solutions the corrosion rate is maintained and spreading may continue till the corrosion attacks, say, 75% of the whole surface in N/10 KCl; nothing like definite pitting occurs, but there is a preferential attack on the crystal boundaries. In 2N KCl the whole surface of the zinc may be attacked.

On zinc very highly purified by fractional distillation the boundaries are not attacked, but etch pits occur on the crystal faces; each face has a characteristically shaped pit. The corrosion rate due to oxygen absorption is not much altered by high purification, though corrosion due to H evolution is cut down.

It is interesting to note that corrosion is more widespread and severe on the bottom than on the top of horizontal discs in N/10 KCl. Fig. 37 (Plate II) shows specimens after 17, 50, and 112 days' corrosion. This might be thought to be an example of the differential aeration principle which postulates most corrosion where there is least oxygen, but it is easy to show that it is not so, and that gravity is the main determining factor. For this purpose the apparatus shown in Fig. 38 was used; the solution entirely fills the inner cap and the capillary tube above the specimen which rests on the points of the glass tripod. The liquid level is halfway up the outside of the inner cap, so that oxygen reaches first the *bottom* of the specimen. Deeper and more corrosion then occurs on the bottom surface, just as when oxygen first reaches the top surface.

In order to ascertain the depth of corrosion penetration, specimens were turned down till all signs of corrosion had disappeared on one face, and the thickness between the turned face and an uncorroded area on the other was then measured. This thickness was then subtracted from the original thickness of the metal. All measurements refer to the greatest penetration observed. In strong chloride solutions the whole surfaces of the specimens may be attacked, and the penetration into the top and bottom surfaces cannot then be determined separately, but only total diminution of thickness.

Approximate rates of penetration in N/10 KCl were determined by dividing the depth of corrosion penetration (expressed in mm.) by the period (in days) over which the time/corrosion curve was linear. The result is multiplied by 1000, *i.e.*, the rates are expressed in thousandths of a millimetre per day.

If a corrosion/time curve was not linear for the whole of the experiment, a correction was made because the rate of penetration presumably fell with a drop in corrosion rate. Consequently, an extrapolation of the linear part of the corrosion/time curve was made to the total corrosion. The corresponding time was used to divide the observed penetration, and so give the penetration rate. This correction was only necessary in

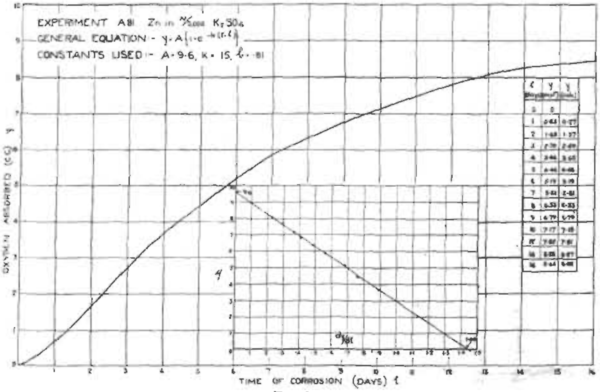


Fig. 35

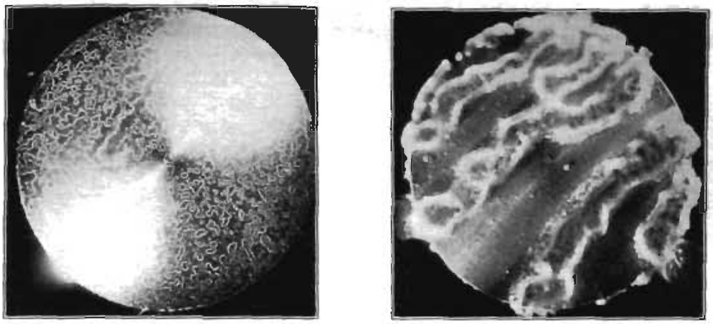
Zinc in N/5000 K_2SO_4

TABLE XI

Average rate of penetration of zinc in N/10,000 KCl

Days corroded	(Days of O absorption => 0·1 c.c. per day	Rate of penetration* Upper S	Lower S	Absolute penetration, mm. Upper	Lower
24	24	18	8	0·44	0·20
50	19	24	10	0·45	0·20
81	21	(28)	22	0·59	0·46
86	22	19	20	0·43	0·45
112	17	23	12	0·41	0·21
117	24	21	11	0·51	0·27
		Mean = 22	Erratic	Mean = 0·47	Erratic

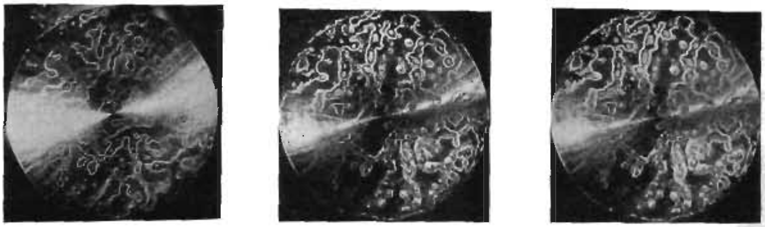
* Expressed as $\frac{\text{mm.}}{1000}$ per day



27 Mins — 5 Days

FIG. 34

Zinc in $N/10{,}000\ K_2SO_4\ (\times 2\frac{1}{2})$



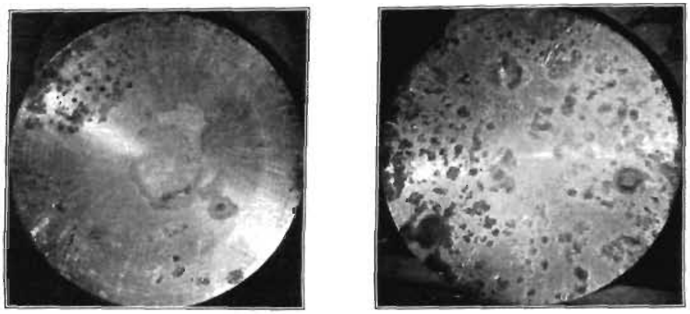
47 Mins — 2 Hours — 3 Hours

1 Day — 6 Days — 6 Days (corrosion products removed)

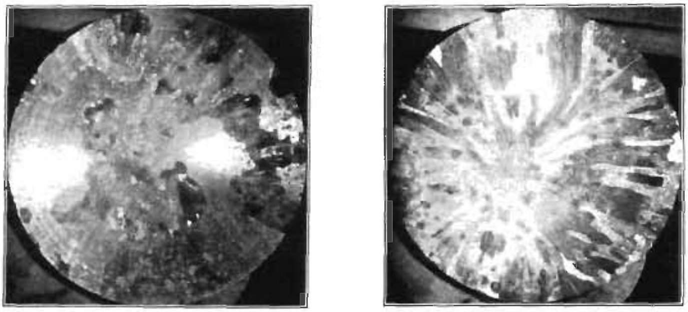
FIG. 36

Zinc in $N/10{,}000\ K_2SO_4\ (\times 1\frac{3}{4})$

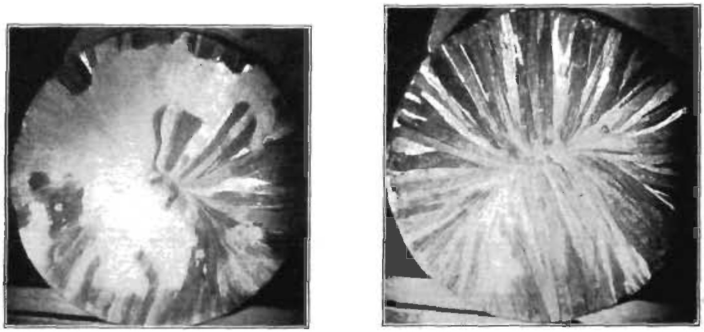
PLATE I



17 Days' corrosion



50 Days' corrosion



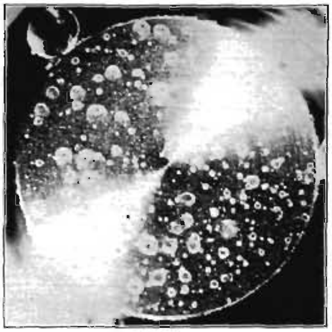
112 Days' corrosion

Tops (× 2½) *Bottoms*.

FIG. 37

Zinc in N/10 KCl

7 Mins.

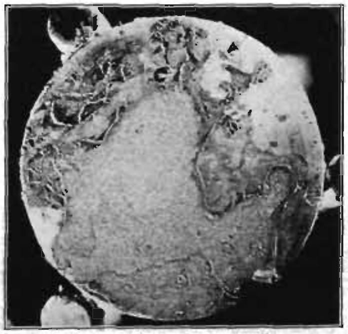


30 Mins.

8 Hours

1 Day

6 Days



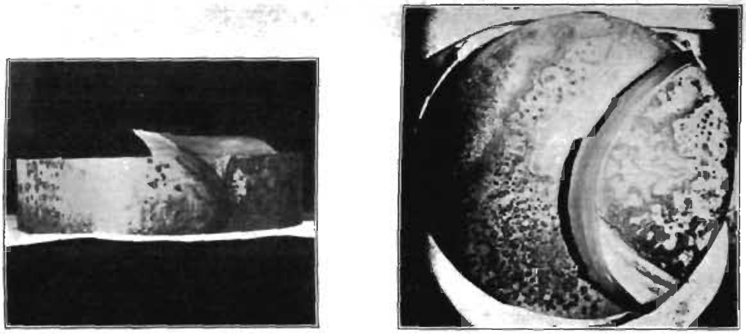
37 Days (corrosion products removed)

FIG. 40

Mild steel in N/100,000 KCl under oxygen

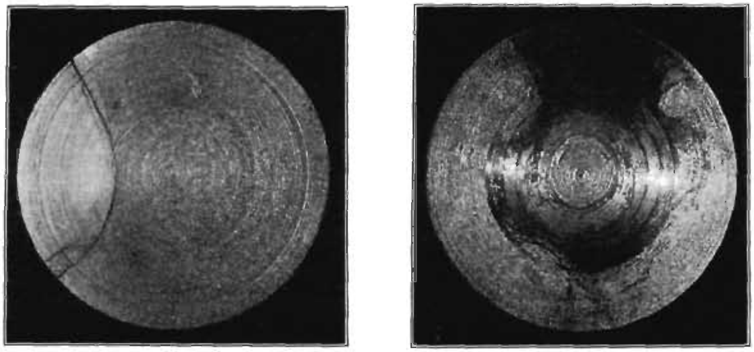
Upper surface (× 2½)

PLATE III

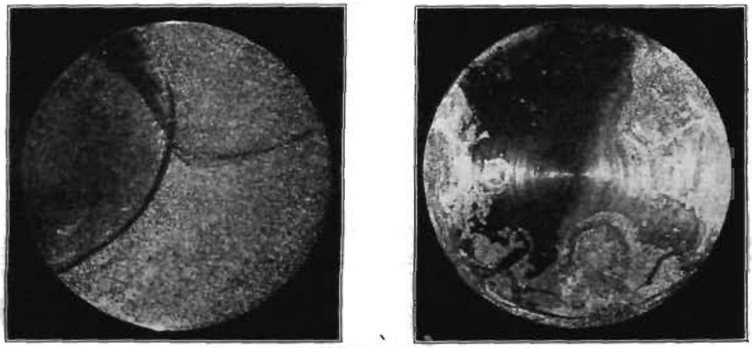


Side elevation (× 2½) Plan (× 2½)

FIG. 41—*Arc-like walls of oxide on steel*



Top 10 Days at 5 atm. *Bottom*



76 Days at 1 atm.

Top *Bottom*

FIG. 44—*Steel in N/10 KCl under oxygen* (× 2½)

xperiments that lasted over 90 days in N/10 KCl and as usually small. Some results are shown in Fig. 39. will be seen that *corrosion was deeper on the lower* urfaces, and that the rate of penetration varied with me in a remarkable way. The rate falls rapidly in a near manner from a maximum of about 20/1000 mm. er day to about 7/1000 mm. in about 30 days, and terwards much more slowly, again in a linear manner. his result, when taken in conjunction with the form the corrosion/time curves, means that corrosion preads rapidly for about 30 days, at the end of which

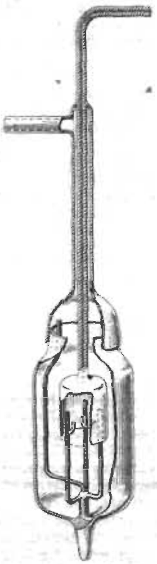


FIG. 38
Inverting apparatus

has almost reached its maximum extension; it then netrates steadily but very slowly about, 5/1000 mm. r day.

For N/10,000 KCl a different method of calculating tes of penetration was used since the corrosion/time rves were nowhere linear. All that can be done is state an average rate of penetration for the whole riod over which at least some small and arbitrarily fined rate of corrosion occurred. This has been ed to correspond with an oxygen absorption of 0·1 c.c. oxygen per day. Any small amount of corrosion curring after this is assumed to contribute nothing the penetration—an assumption that probably troduces a negligibly small error. The results are own in Table XI. Note that the rates are higher than ose in N/10 KCl, although the method of calculation is biassed against them; also that *the greatest* rate and depth of penetration occur on the *top* surface of the specimen.

It is now clear that the maximum rate of penetration is obtained in the initial periods of experiments in quite dilute solutions such as N/10,000 or less, but the maximum absolute depth of penetration that can be reached in prolonged periods is obtained in stronger solutions such as N/2. The reason for the high initial rate in the weaker solutions seems to be that the area attacked is dictated by the concentration of chlorine ions, and in weak solutions is small relatively to the available oxygen supply; penetration is therefore rapid, but the rate *soon falls owing to lack of chloride in the small laboratory* vessels used. In stronger solutions the area attacked is greater and penetration slower but the rate can be maintained, so greater absolute pentration occurs.

Finally, it should be noted that there is no sharply isolated pitting on any of the zinc specimens except those exposed to conductivity water and very dilute solutions; nor does pitting occur on mild steel in N/10

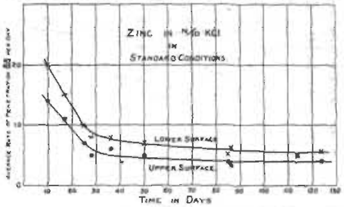


FIG. 39
Curves for rate of penetration

and stronger KCl and NaCl solutions in our standard conditions of immersion, but corrosion is spread over wide areas. The distribution of pitting in conductivity water can be easily changed by a change in the conditions, for instance by introducing convection currents set up by temperature variations across the corrosion vessel. Fig. 33A shows that a radial distribution then occurred in conductivity water exposed to the atmosphere, instead of the sporadic distribution referred to earlier. This proves that a factor external to the metal itself may be the determining factor of the loci of pits.

DISTRIBUTION OF CORROSION ON MILD STEEL

Many, but not all, of the facts are similar to those for zinc; they may be conveniently summarized in the following six statements:

(1) *The starting points of corrosion were sporadically distributed and very numerous*; in our standard procedure about 10,000 per sq. cm. were visible after 2½ minutes even in N/10,000 KCl, and far too many to count in N/10. Probably they correspond to atoms that have not become associated with oxygen during exposure to the atmosphere, but were specially reactive owing to the process of preparing the surface and other factors. They occur especially at edges, burrs, contacts with the glass points and chemically specialized areas; very slight physical or chemical differences are sufficient to determine their positions. On highly-purified iron the

number of centres is less, but the corrosion rate is not much altered.

(2) *There was usually a cessation of corrosion*, after an hour or two, at a very large number of the points, but persistence at others which seemed to be fairly sporadically distributed. The cessation appeared to be due to suppression of the less active points by films formed by alkali resulting from action at the most active (see *Fig. 40, Plate III*).

(3) *A process of aggregation began after a few hours which resulted in the formation of a few large attacked* and unattacked areas. These were continued round the discs from one surface to another, owing, no doubt, to the creeping of alkali

(4) *The configuration of the corroded areas was decided* early in the process in dilute solutions and spreading thereafter was very slow, probably owing to the formation of impervious walls between the attacked and protected areas, which hindered interaction of corrosion products close to the metal surface.

(5) *Spreading increases with concentration*: in N/10

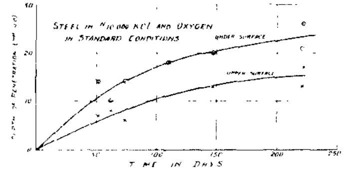


Fig. 42

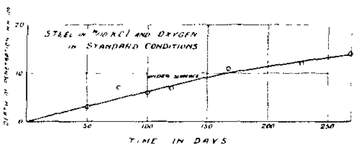


Fig. 43

KCl arc-like impervious walls may still occur (see Fig. 41, Plate IV) but are too local to prevent spreading over as much as 75% of the whole surface; in N/2 and stronger solution the whole surface may be attacked, *but in N/10 corrosion was more widespread on the top* surfaces than the bottoms.

(6) *Penetration is deeper in dilute solutions (such as* N/10,000) for periods up to about one year. Since corrosion in these solutions ceases much sooner than in stronger ones (such as N/10) penetration will *eventually* be deeper in the latter, but only after several hundred days.

The depth of penetration was usually found to be greater on the bottom surfaces of steel, and specially deep at or near the position of the glass points which supported the specimen. Rates of penetration are shown in Figs. 42 and 43.

Factors which Control Distribution

The distribution of corrosion is closely associated with the distribution of alkali which tends to creep over the whole surface of the metal and produce protective films where it is in excess, but is neutralized by metallic salt produced at reactive areas on the metal. The heavy metallic salt tends to fall rather than creep; hence, gravity is an important factor in determining distribution and penetration. In long-continued experiments in strong solutions at standard depth corrosion is greater in amount and more widespread on the top surface of a horizontal steel disc, but deeper on the bottom surface; *this result is largely due to the tendency of the heavy metallic salt to fall directly down, along, or away from the surface of the specimen.* With very shallow immersion the top surface is largely protected because of the relatively high concentration of alkali there, but if air be substituted for oxygen, most corrosion always occurs on the top, since alkali protection is less effective in air.

I showed a little while ago that corrosion was more widespread on the bottom surface of zinc in standard conditions, and not on the top as with steel. While, therefore, a simple explanation of the distribution based on differences of oxygen concentration is clearly invalidated, should not also be any explanation based on gravity effects and film distribution?

This is not a necessary consequence because the properties of the material forming the protective layers *on the two metals are not identical. Corrosion,* no doubt, starts up rapidly at many points over the two surfaces of both metals, but in chloride solutions the hydroxide film is not so protective to zinc as to steel Zinc steadily passes into solution through the gradually thickening and slightly porous film which becomes undercut and so loses adhesion; it is, therefore, steadily pulled off by gravity from the lower surface, but not from the top. Moreover, the continued corrosion on the bottom will, so to speak, count two on a division, since it will use up some of the oxygen, and increase alkali production, on the partially protected top surface This is an example of a rather general principle that rapid corrosion anywhere will damp down corrosion somewhere else, either by seizing most of the available *oxygen or by causing the formation of protective films.*

On steel, since the cathodic film is much more protective it remains very thin, and is not undercut; gravity cannot pull it off and the bottom surface of the steel remains relatively protected for long periods, except where contact with glass points or the spreading of metallic chloride from the top surface round the specimen interferes with the film; corrosion begins rapidly on the top surface where there is a large oxygen supply and, no doubt, assists in the protection of the bottom. The continued corrosion on the top is due to intimate mixing of alkali and metallic salt since both tend to spread sideways over the surface; on the bottom the metallic salt falls directly down, leaving the alkali to spread out and protect the surface. Therefore, gravity tends to spread corrosion on the top surface and localize it on the bottom. The influence of glass points and some other foreign *materials in localizing corrosion is* probably due to surface tension factors which cause films to cling to the glass etc. rather than to the metal.

The reactive areas on mild steel often seem to lose their special activity quite early in the corrosion process; any permanent influence they may have on distribution is indirectly exerted through the spreading tendencies of

alkali, and the building up of walls of mixed oxides round corroding areas, which tend to hinder spreading. A relatively impervious type of wall has been observed: (1) in very dilute KCl solutions (up to N/5000) in standard conditions, (2) in N/10 KCl in conditions of very shallow immersion, (3) in N/10 KCl after very long periods of immersion (650 days) in standard conditions. As long as such walls do not build up into domes which cover the whole specimen and stop all action they tend to localize corrosion, since they tend to localize the alkali which accumulates and protects the metal outside them; but they may also slow down the whole process by forming dome-like structures over corroded areas which prevent the egress of ions. Thus, with very thin metal, a race might occur between cessation of corrosion with the complete closing of the domes, and penetration of the metal. The rate at which such walls are built up will, no doubt, vary with different solutions and conditions; thus, in very dilute solutions the substitution of air for oxygen prevents their formation, at any rate for a long time.

Convection currents may have an important effect on the distribution of corrosion which they exert partly through influence on the physical condition of the corrosion products and partly through the distribution of alkali.

An increase in the rate of oxygen supply obtained by increased pressure does not alter the distribution of corrosion appreciably up to 10 atmospheres at least, as shown in Fig. 44 (Plate IV). Dissolved oxygen does not seem to act as a passifier up to 120 atmospheres at least, but always increases corrosion rates wherever it obtains access to the metal.

Effect of a film-forming solution.—A very dangerous type of pitting may occur on steel in mixed solutions of chlorides and alkali such as (0·06 N KCl and 0·04 N KOH). This solution causes a protective film to form on mild steel, provided that certain foreign bodies do not come in contact with the film-covered surface of the metal; but contact with glass or silver sand, owing to physical causes, brings about failure of the film and starts corrosion; pits may then be formed which will penetrate deeply. The precipitated oxides formed over the pit are freely permeable to ions, while the excess alkali and the formation of hard crusts prevent corrosion spreading; the result is that a total penetration of 3·2 mm. in 3 months may occur in our standard conditions. In N/10 KCl in similar conditions a penetration of only 0·11 mm. occurred in the same time, *i.e.*, about 1/30, though the total amount of corrosion was the same in the two solutions. In N/10,000 KCl the penetration reached about 0·18 mm. on the under surface and 0·13 mm. on the top in the same time.

It should be noticed that no importance is attributed to the question whether or not oxygen penetrates freely into the pits. The assumption is usually made that it does *not* do so, because of the presence of corrosion products over the pit; since, however, ions can freely pass through these deposits (or corrosion would cease) it is at least probable that dissolved oxygen can also do so; it is better therefore to make no assumption on the point and to abandon the common idea that differential aeration caused by deposits is an ordinary cause of pitting on totally immersed metal.

Conditions which generally favour pitting are:

(1) The presence of a protective, but conducting, film over a relatively large part of the metal surface. Such a film may be formed previous to any wet corrosion, *e.g.*, mill scale, or it may be formed by the corrosion process itself, or by some precipitation process not depending essentially on corrosion.

(2) Some factor which will *locally* destroy the film, such as the presence of a suitable foreign substance, relatively difficult access of alkali or other suitable film maintainer, alternate wetting and drying, or gravity; the destructive factors may be different for different films.

(3) Any precipitated corrosion product formed in and over the pit must allow passage of ions.

(4) Sufficient oxygen must enter a pit on iron or steel to prevent the formation of an obstructive film of ferrous hydroxide at the anode. A small amount will probably suffice.

No. 3 has been a rather neglected subject of investigation, but it seems to me that changes of corrosion rates are sometimes due to changes in the amounts and/or properties of masses of corrosion products formed over anodic areas, a simple "oxygen screen" view of their effect is certainly insufficient.

It may, at first, seem curious that a condition for pitting is the protection of a large part of the metal surface, but the explanation is simple. Oxygen reaching the film-covered metal cannot be used for corrosion locally since metal ions cannot pass into solution there, consequently it is available to depolarize the hydrogen displaced by metal entering solution elsewhere, where there is no protective film. If oxygen penetrates into a pit it will cause local corrosion in it to just the same extent as if it did not penetrate but reached the film outside. Provided always that the protective film outside the pit remain intact, oxygen penetration is of no consequence. Actually, more oxygen probably reaches the metal in the pit than the metal-surface outside, since the latter is covered with a protective film through which only electrons can penetrate at an appreciable rate, and a correct quantitative statement about the differential aeration becomes difficult and is therefore best avoided. In any case, differential aeration only affects distribution indirectly through local production of alkali and protective films: if little or no alkali is formed during the corrosion process most corrosion occurs where there is most oxygen.

From this discussion it seems clear that the causes of pitting are often to be found in the conditions to which the metal is subjected rather than to any factor in the metal itself. Nevertheless, the effect of composition cannot be altogether excluded; for instance, sulphur in steel is commonly thought to be a cause of increased and localized corrosion and its exact effect is now being studied by the Iron and Steel Institute Corrosion Research Committee. It may turn out that the total amount of corrosion is not affected, but only its distribution, which may be influenced by local film failure, or by increased local reactivity, perhaps due to local supersaturation with sulphur compounds. With certain light alloys, however, impurities may increase both

total and local corrosion since the corrosion rate is not controlled by the rate of oxygen supply, but by the operative differences of potential.

The Effect of Partial Immersion on Distribution

So far we have only considered the distribution of corrosion on specimens wholly immersed in stagnant

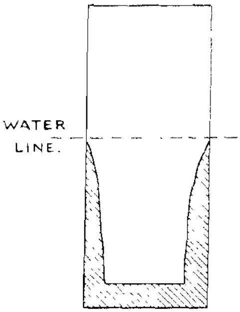


Fig. 45

"Ideal" distribution in KCl (U. R. Evans)

liquids, and we have seen that differential aeration is not usually an important determining factor.

Metals are also used in conditions of partial immersion, and it is interesting to study the distribution which results. Evans and Hoar have shown that most of the hydrogen depolarization on steel, partially immersed in N/100 KCl, occurs over a strip along the water-line only 2 mm. wide: in their narrow, thermostated vessels only a little oxygen penetrated into the body of the liquid, so that a high degree of differential aeration occurred; here, if anywhere, the influence of this factor ought to be predominant.

The distribution on the small, emery-ground specimens of steel sheet used by Evans and Hoar was as shown in Fig. 45. There was a protected band along, and below, the water line, which extended, in the centre of the specimen, for some distance downwards. Corrosion occurred along most of the three immersed edges. The experiments were only continued for 2 to 4 days, and since it is known that distribution often undergoes changes with time, we have examined at Teddington the effect of longer times of immersion in N/2 NaCl beneath oxygen at 25° C. using specimens 15 cm. long. The results are being described in detail elsewhere. [Proc. Roy. Soc. **A.** 1933.]

The distribution of corrosion on both the steel and zinc specimens seems to be dictated by at least four factors, namely:

(1) The distribution of films of corrosion products possessing protective properties which might be either long-continued (with steel) or ephemeral (with zinc).
(2) The tendency of alkali to creep away from its principal seat of formation (at and near the water-line) down into the interior of the liquid, and so cause protection there.
(3) The special reactivity of edges, at which corrosion started and then spread inwards at varying rates; spreading could take place towards either more, equally, or less aerated parts of the metal.
(4) The tendency of heavy metallic salt to *fall*, and so to neutralize alkali and cause corrosion to spread *downwards* from a given starting point.

The very high degree of differential aeration influences the distribution indirectly through the production of alkali at the most aerated places, but this influence can be locally overruled by other more powerful factors, such as the creep tendency of alkali and the downward spreading from initial centres.

The special tendency of the edges to corrode is, no doubt, due to the difficulty of making the edges of emery-ground specimens exactly like the faces. Thick milled specimens can be made much more alike all over, and there is then less tendency for corrosion to begin at the edges.

It should be noted that the protected area shown in Fig. 45 is most definite in thermostated conditions with an atmosphere of oxygen. In ordinary "service" conditions these protected zones are usually absent owing to the destruction of the protective film, probably by the action of the air and alternate wetting and drying, and heavy waterline corrosion occurs in the most highly aerated regions.

Even in unthermostated laboratory conditions, N/2 NaCl often attacks steel right up to the waterline: in London tap water there is a narrow protected zone, about 2 mm. wide.

The general view of the distribution of corrosion given in this lecture is based on the idea that dissolved oxygen is a stimulator of corrosion, not an inhibitor or passifier as is sometimes stated, and I think that all available experimental evidence shows that it does act in this way whenever it is not denied access to a metal surface by the presence of air-formed or precipitated films; thus high oxygen pressures have been shown to stimulate corrosion in N/10 KCl, not to inhibit it.

Whenever oxygen appears to produce local passivity at highly differentially aerated places, the effect is really due to a secondary, film-forming action, which is dependent on the nature of the solution and the conditions of immersion: in some solutions, such as NH_4Cl it does not occur at all: in others, it only occurs in special conditions. Owing to the large number of special explanations required, it seems best to abandon the Differential Aeration principle of local action and pitting as a useful general statement, and substitute for it a "film distribution view" of corrosion. The two sometimes give similar interpretations, but the latter is the more generally applicable and draws attention to the actual passivifying factor; in addition, we have merely to remember that local passivity can usually stimulate corrosion elsewhere since it does not use any appreciable proportion of the available oxygen supply.

The work on which this lecture has been based was carried out at the Chemical Research Laboratory, Teddington. Much of it has been published in the Proceedings of the Royal Society which has kindly granted permission for the reproduction of many of the figures. The director of the laboratory, Prof. G. T. Morgan, F.R.S., has placed many facilities at the disposal of the investigators, who have included

Mr. J. M. Stuart, Dr. A. R. Lee, and Dr. F. Wormwell. The last named has taken an active part in the preparation and presentation of the lectures at all the centres where it has been given, and I take this opportunity of thanking him for his able assistance.

PLASTICS INDUSTRY EXHIBITION, 1933

During the past six or seven years it has been the practice at the Science Museum to set apart a gallery in which scientific institutions and related bodies could exhibit the results of researches and their practical applications. These exhibitions, arranged co-operatively, have met with great success, as is instanced in the case of recent exhibits showing the history of the artificial silk industry and the principles and applications of modern optical instruments.

Latterly however, it has been found that the expense incurred is in many cases rather more than can be borne with comfort by individual institutions. The question has therefore arisen as to whether industry generally would be prepared to take advantage of similar facilities if these were placed at their disposal. In this case the exhibitions would be arranged primarily from the point of view of the industry concerned and would aim at illustrating to other industries the use that could be made of their materials. Though in part an industrial movement it would nevertheless be in keeping with the times and serve to show the modern applications of science on a scale larger than could be employed in any permanent collection.

As a beginning, the British plastics industry has accepted an invitation to arrange an exhibition on a comprehensive scale giving a clear view of all branches of pure and applied "plastic" practice. The exhibition will be opened by the Rt. Hon. Lord Irwin, K.G., G.C.S.I., G.C.I.E., President of the Board of Education, on Wednesday, April 5. The floor space occupied will total approximately 10,000 sq. ft., so that it will be seen at once that a determined effort is to be made to present a complete picture of the various activities of the industry.

Though in the nature of a first experiment, success should be assured from the fact that the organization is in the hands of a capable committee embracing both trade and research institutions, working in collaboration with the Science Museum. It is significant that the Plastics Group of this Society is undertaking an important share of the exhibition arrangements and is also organizing a series of lectures. Further details of the work accomplished will appear later. From an industrial standpoint the results obtained should prove of great interest in determining the value of inexpensive and reasonably wide exhibition facilities in London. Dependent on these results there is little doubt that facilities might be extended later to other industries.

The exhibits will be arranged on two floors of the Museum. In the entrance hall, on the ground floor, will be an attractive display of a character calculated to appeal to the general visitor. It will include illustrations of research and of plant and some of the finest products of the moulding trade. This will serve as an introduction to the main exhibition which will be arranged from an industrial standpoint on the third floor, chiefly in gallery 66, from which the Chemistry Collections have temporarily been withdrawn for the purpose. Here will be grouped all phases of the industry commencing with a series of cases devoted to the more significant results of research as pursued at the Chemical Research Laboratory of the Department of Scientific and Industrial Research.

Raw materials, intermediate products, and the moulding powders from which finished "plastics" are produced will be represented in groups organized by the Society of Chemical Industry. Moulded articles and plant of all kinds will be arranged through the British Plastic Moulding Trade Association. One of the largest groups of exhibits is almost certainly to be devoted to moulded articles of which there is an infinite variety. Objects of plastic ware such as the new-pattern telephones and non-fragile domestic appliances now excite little comment, while no less important articles range from automatic fire alarms, house meters, and a host of other electrical instruments and fittings to door furniture, motor accessories, and fancy goods. The relatively new technique of using laminated plastic sheets will be illustrated on an imposing scale by a specially-designed room in which doors, wall-panelling, and other effects will be rendered in laminated material.

During the period of the exhibition a series of lectures by experts in the various branches of plastic technique will be given in the Museum lecture theatre at times and dates to be announced elsewhere. The theatre is fully equipped for experimental lecturing, and use of these facilities will in many cases enhance the interest of the lectures given. A. BARCLAY

BICENTENARY OF JOSEPH PRIESTLEY

The 200th anniversary of the birth of Joseph Priestley was commemorated last week-end in Leeds. On Saturday, March 11, the Old Boys' Association of Batley Grammar School, where Priestley was a scholar, held a dinner at which the toast, the "Memory of Priestley," was proposed by Mr. T. C. Taylor, who referred to the outstanding need to-day in modern industry, and particularly at the strategic points of the woollen trade, of men of Priestley's adventurous spirit and inquiring turn of mind. On Sunday, March 12, special sermons on "Priestley's Contribution to Thought," and "The Life and Personality of Joseph Priestley," were given at Mill Hill Chapel, where Priestley was pastor for six years, by the present minister, Rev. W. L. Shroeder. On Monday, March 13, in the Priestley Hall, Leeds, Miss Anne Holt, the author of a recent biography of Priestley, spoke on "Priestley's Life and Work." Earlier in the evening, a commemorative meeting of the Priestley Club was held at the University of Leeds, when Prof. Irvine Masson (Professor of Chemistry, University of Durham) delivered a lecture on "The Discovery of Gases, and its Significance," to a large audience. Prof. Masson briefly described the state of chemical knowledge up to the time of Priestley, and pointed out how Priestley's work laid the foundations of the atomic theory and of the modern conceptions of the structure of matter. The Priestley Club invited chemical organisations having local sections or representatives to participate in this celebration, and many

responded to the invitation. After the lecture, the club held its usual dinner, at which the following guests were present: Mr. J. A. Craven, chairman of the Yorkshire Section of the Society of Chemical Industry; Prof. F. Challenger, chairman, the Institute of Chemistry (Leeds Area Section); Mr. H. S. Patterson, member of Council of the Chemical Society; Prof. F. M. Rowe, representing the Society of Dyers and Colourists; Mr. Skinner, chairman N.E. Section of the Institute of Brewing; and Mr. F. C. Thompson, president of the International Society of Leather Trades Chemists. The toast of "Priestley" was proposed by Mr. J. C. Gregory, who gave a graphic account of Priestley's personality and of his contributions to chemistry.

Dr. J. T. DUNN

This year the Society holds its annual meeting in Newcastle, just 50 years after the amalgamation of the Newcastle Chemical Society with this Society. It will be regarded by every member of the Society as particularly fitting that the president for 1933–34 will be Dr. J. T. Dunn, a Newcastle man, and one, moreover, who took an active part in effecting that amalgamation of 50 years ago.

The Society may be said to have its roots in Newcastle. So has Dr. Dunn, for he was born there 75 years ago. In 1873 he became a student at what is now the Armstrong College, graduating in 1877, the year in which he joined the Newcastle Chemical Society. At the same time he became the first Pemberton Fellow of Durham University, and demonstrator in chemistry and physics. In 1880 he became honorary secretary and editor of the Transactions of the Newcastle Chemical Society, taking part in the negotiations which led to its amalgamation with this Society in 1883. From this time he was prominent in the affairs of the Newcastle Section, continuing as honorary secretary for the next 11 years, serving as chairman in 1903—05 and 1930—32 and is now vice-chairman. He has served on the Council of the Society for many years and has also been a vice-president.

We have not space here to give more than the briefest outline of a career that has been remarkably active. After some years at the Gateshead School and later as principal at the Northern Polytechnic, Holloway, he returned to Newcastle in 1901 to join the old-established analytical and consulting business of J. & H. S. Pattinson, of which he became sole principal in 1912 on the death of John Pattinson. As an analyst he has held many public appointments, and the Society of Public Analysts honoured him by election to its presidency in 1930–32. He has served also the Institute of Chemistry both on the Council and as an examiner, and has been a Fellow of the Institute since 1901. In addition he has worked on committees of the British Standards Institution, the North-Eastern Coalfields Survey, and many other bodies, whilst he has found time to write two text-books and to take an active part in the administration and educational affairs of Newcastle. His active life has been worthy of a president of this Society. Whilst there may be some who would dispute his claim to be called the G.O.M. of chemistry in this country, it is certain that none can match his part in the history of chemical associations here.

SOCIETY OF CHEMICAL INDUSTRY

OFFICIAL NOTICES

Annual Reports. The new volume of the Society's Annual Reports on the Progress of Applied Chemistry 1932, Vol. XVII, is now ready. Copies may be obtained by postal application to the General Secretary, 46, Finsbury Square, London, E.C.2, and must be prepaid. Members 7s. 6d., non-members 12s. 6d.

MEMBERS ELECTED

March 10, 1933

Bowen, George Henry, "Brynton," Harboro Road West, Sale, Manchester. Chemical Engineer.

Brock, Stanley, Stanley Brock, Ltd., Winnipeg, Manitoba, Canada. President.

Clulow, Frederick W., 25, Broadhurst Gardens, S. Hampstead, N.W.6. Science teacher.

Cote, Jean, 4075, Cartier Street, Montreal, P. Que., Canada. Chemist.

Crowle, Donald Percy, Chatsworth Hotel, Leinster Square, Bayswater, W.2. Student.

Darney, Alexander, 12, Joinings Bank, Langley Green, Birmingham. Works chemist.

Dow, William Thornton, c/o Messrs. De Bruyn, Ltd. Unilever House, Blackfriars, E.C.4. Advisory and research chemist.

Fitter, Frederick Leonard, 15, Manor Park, Lewisham, S.E.13. Works manager.

Ford, Walter Percy, c/o The British Arkady Co., Ltd., Skerton Road, Old Trafford, Manchester, 16. Chemist.

Giordani, Prof. Francesco, Labo di Elettrochimica e Chimica Organica della R. Scuola Superiore d'Ingegneria, Via Mezzocannone, Napoli (Italy). Professor of chemistry.

Glynn, H. E., c/o C. C. Richardson, Esq., Rivadavia 3042, Buenos Aires, Argentina. Chemist-in-charge.

Goldberg, Alan August, Messrs. J. R. Crompton & Bros., Ltd., Elton Paper Mills, Bury, Lancs. Research chemist.

Hobson, Joseph Edward, c/o Messrs. Joseph Hobson & Son, Ltd., Regent Street, Leeds. Wine merchant.

Kagan, Abraham, 51, Park Drive, Acton, W.3 Analytical chemist (technical director).

Laughton, Arthur, Messrs. Peerless Refining Co., Ltd. 59-71, Cheapside, Liverpool. Works chemist.

Luke, John Kenneth, "Quenby," Clifton Drive, Fairhaven, Lytham, Lancs. Sales engineer.

Marshall, Thomas, c/o Messrs. Achille Serre, Ltd. Cleaners and Dyers, Blackhorse Lane, Walthamstow E.17. Works chemist.

Menne, W. A., c/o British Glasurit, Ltd., Church Wharf, Chiswick Mall, London, W.4. Director.

Mobley, Roy Lee, 1309, Flowerdale Lane, Baton Rouge Louisiana, U.S.A. Assistant biochemist and bacteriologist.

Puleston, Ronald, 25, Cottenham Park Road, Wimbledon, S.W.20. Chemist.

Ray, Dr. A. B., Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N.Y. Chemical engineer.

Shepherd, Arthur Frederick, 13, Norland Square Holland Park, W.11.

Streatfield, Edward Leslie, The Colne Valley Water Co. Aldenham Road, Watford, Herts. Research chemist and chemical engineer.

Taylor, Ernest, The Harris Institute, Corporation Street, Preston. Lecturer.

Taylor, Joseph Allen, "The Haven," Montpelier Avenue, Bispham, Blackpool. Chairman, J. Spencer & Co., Fleetwood, Ltd.

Thornley, Basil D., 39, North Park Road, Bramhale, Cheshire. Research chemist.

Viterbi, Ing. Adolfe Ottolenghi, Soc. Montecatini Via Principe Imberto 18, Milan (Italy). Technician.

Westman, L. E., 366, Adelaide Street, W. Toronto 2, Ontario, Canada. Publisher, "Canadian Chemistry and Metallurgy."

GLASGOW SECTION

The annual business meeting of the above Section was held in the Royal Technical College, Glasgow, on Friday, March 3. Prof. F. J. Wilson occupied the chair.

The hon. secretary and treasurer, in reading a report of the work of the Section during the past year, dealt with the outstanding meetings of the session, namely, the visit of the Chemical Engineering Group on November 4, 1932, and the Jubilee Memorial Lecture on November 25, 1932. He also explained the work that was being done by members of the Section in connexion with the Scottish National Development Council. As a result of the Section's activities a technical committee had been set up to inquire into and report on the present conditions and future prospects of the chemical industries in Scotland.

Mr. Ramsay, the representative of the Section on the Board of Directors of the Glasgow Chamber of Commerce, presented his report and explained briefly the manifold activities of the Chamber of Commerce during the past session.

After the re-election of the present officers and members of committee, two new members of committee, Dr. J. Weir and Mr. G. T. MacLeod, were elected on the motion of Messrs. Skilling and D. A. MacCullum to the places vacated by the retiring members, Messrs. R. G. W. Eadie and P. P. Moulton.

At the conclusion of the business meeting a joint meeting with the Institute of Chemistry was held. Three cinematograph films, "The Story of a Piece of Paper" (lent by Wiggins, Teape & Co.), "Modern Asphalt Pavements" (lent by Highways Construction), and "The Manufacture of Aurora Lamps," were exhibited to the accompaniment of a radio-gramophone. Mr. Osborne, the managing director of Aurora Lamps, Ltd., explained points in connexion with the manufacture of electric lamps and kindly answered questions which were raised by members of the audience.

LONDON SECTION AND PLASTICS GROUP

There was a good attendance at the joint meeting of the London Section and Plastics Group of the Society, held on March 6 with Dr. G. Monier-Williams, chairman of the London Section, presiding, when a paper on "Plastics with Special Reference to Cellulose Materials," was read by Dr. W. J. Jenkins of the Technical Department of Imperial Chemical Industries, Ltd.

Dr. Jenkins pointed out that it was customary to refer to plastics made from cellulose derivatives as "Cellulose Plastics." The term "cellulose" in this connexion was not scientific and included such diverse substances as nitrocellulose and ethyl cellulose. There was also considerable difficulty in defining the term "plastics"; to obtain a detailed knowledge of the laws underlying the different types of flow required a good deal more exact work than was yet available. There was general agreement on the distinctions between the following: (*a*) instantaneous elastic deformation which disappears immediately the stress is suppressed; (*b*) the reversible deformation which is a function of time; (*c*) viscous flow which is irreversible. Plasticity was related to the capacity of a material for being moulded into a given form and to the capacity for retaining this form. Further, it would be appreciated that all three classes of deformation entered into every case of plastic flow, and into all measurements of tensile strength of plastics. Such properties as hardness, resistance to abrasion, and brittleness were each related in some way to the manner in which the substance responds to the laws of flow. The lecturer then put forward a useful tabular classification of plastics, the first subdivision of which dealt with thermoplastics including the cellulose derivatives, being those materials which became softer as the temperature was raised, and remained in this condition while the temperature was constant. Thermohardening materials occupied the second subdivision of the table, and were such that with continued heating they became harder and eventually became infusible. In the third subdivision were included materials which were hardened by chemical treatment, of which rubber, which could be hardened by vulcanization, was an example. The fourth subdivision represented a class of materials which become hardened at relatively high temperatures and which it was not customary to include among the thermohardening type of plastics.

The most important of the cellulose derivatives included in the first subdivision were nitrocellulose or cellulose nitrate, cellulose acetate, ethyl cellulose, benzyl cellulose, and the lecturer stated that he proposed to give an idea of the special properties of other cellulose derivatives by comparing them with nitrocellulose. In this connexion he said:

The use of cellulose to the extent with which we are familiar, particularly in the form of cotton in the textile industry, is due more to its high tensile strength than to its chemical properties. This quality is illustrated by tensile strength figures (Mark, Trans. Far. Soc., 1933, **29**, 6) which show that the tensile strength of good quality cellulose is superior to that of most metals, being higher than that of copper and inferior only to good quality steel and a few of the heavy metals. This factor deserves attention in relation to the use of cellulose derivatives in plastics.

The empirical formula for cellulose is $(C_6H_{10}O_5)_n$ where *n* is a number not easily determined. The model of the cellulose unit is now well known and a good deal of the structure of cellulose has been elucidated. It has been established that cellulose is built up of chains of molecular units. These chain molecules consist of glucopyranose molecules linked together through the positions 1 and 4 (Haworth, Trans. Far. Soc., 1933, **29**, 15). The units in the length of chain are linked by primary valencies. The lateral linkage of the chains are due to cohesional forces which are usually referred to as the Van der Waal forces. These forces vary with the

position of the different radicles in the cellulose unit and are not nearly as strong as the primary valency force. Evidence has been put forward to the effect that the long chain molecules are of various lengths and contain about 150–200 glucose units in cellulose samples which have been carefully treated. Any physical or chemical treatment of the fibre decreases the chain length rapidly. The tensile strength of a fibre depends mainly on strength of the chains and also on the manner in which these are interlocked, and as the number of chains passing through the cross-section of a single fibre of ramie cellulose is of the order of one thousand million, an appreciation can be obtained of the nature of the high tensile strength of cellulose.

The cohesional forces seem to hold the chains together in bundles which are not well defined so that a natural fibre of cellulose can be pictured as being built up of a large number of bundles in which the chain lengths are parallel: the bundles are placed at random relative to each other and the spaces between them are filled with unorganized chain-molecules. These bundles are termed micelles. The nature of the cohesional forces between chain-molecules and the interlocking of the chain-molecules make the micelles rigid.

If a fibre of cellulose regenerated from cellulose solution in cuprammonium, for instance, is stretched while in the swollen state, the fibre increases in strength and the chain molecules are oriented parallel to the direction of stretching (Mark. Trans. Far. Soc., 1933, **29**, 7). This flow is somewhat similar to that of a poly-crystalline metallic wire where there is orientation of elementary crystals due to the slip along interior planes, but is different to the extent that there is no sign of disintegration of the structure of the assemblages of chain-molecules during the process. An effect, similar to that referred to above for cellulose fibre, is also obtained during the stretching of cellulose films such as cellophane. Although cellulose is to the degree indicated above plastic it does not undergo plastic flow when heated. In other words cellulose is not thermoplastic. The Van der Waal forces of the radicles hold the chain-molecules so firmly together that the increase in the kinetic energy of the units, due to rise in temperature, is not enough to tear the chains free from each other. Before temperatures sufficiently high for this to happen are attained disruption of the fibre occurs and by-products or cellulose are obtained. Consequently, cellulose does not melt nor can it be distilled.

In the preparation of industrial nitrocellulose, cotton linters are most generally employed, these being the short fibres left after the cotton for textile uses has been removed from the cotton seed. Raw linters cotton contains, in addition to cellulose, moisture and small traces of wax, fat, resin, traces of nitrogen, and mineral matter. After the dust has been removed the raw cotton linters are submitted to a boiling process with caustic soda solution under pressure in order to remove natural oil and non-cellulosic matter. After this treatment the linters usually are bleached, and the linters are then opened up on a teasing machine. Most cellulose, as supplied, contains generally about 8% moisture, and it is desirable to reduce this to less than 1% by stove drying. It is then ready for esterification or etherification, as the case may be. A brief description of the preparation and manufacture of nitrocellulose will give an idea of the esterification process to which cellulose has to be submitted.

Nitration

The two most important processes are the dipper process, and the displacement process.

In the first process the cotton is carefully introduced into a large excess of mixed nitric and sulphuric acids contained in an iron or rustless steel vessel fitted with stirrers. The temperature and time of nitration are carefully controlled, and when the nitration is complete the charge is dropped from the nitrating vessel to a centrifugal. This separates the nitrocellulose from the acid, the latter being run to acid tanks where it is revivified by the addition of known quantities of concentrated acid. The nitrocellulose in the centrifugal is discharged into cold water drowning tanks. In these it is thoroughly washed with cold water and then submitted to a further stabilizing process.

The displacement process of nitration was devised and patented in 1903. The fundamental difference between this and other processes lies in the manner in which the nitrocellulose is freed from acid after nitration. Instead of a sudden drowning of the acid nitrocellulose in a large volume of water, an extremely slow displacement is effected by allowing water to flow in slowly at the top of the nitrating pan while the spent acid is withdrawn at the same rate below. The cellulose is nitrated in wide, shallow, earthenware pans, in a large excess of acid. After nitration the waste acid is allowed to run off, and water (cooled if necessary) is run on the top of perforated plates placed over the cellulose.

Stabilization.—The nitrocellulose, after preliminary boiling with water, is subjected to a special process for reduction of viscosity and further stabilization. The process of stabilization is one of the most important in the manufacture of nitrocellulose, and it was to lack of knowledge of the principles underlying stabilization, and the thoroughness with which this must be carried out, that many of the difficulties in the early history of the manufacture of nitrocelluloses were due. Even to-day the rapid degradation of certain lacquer and enamel films may be partly attributable to the use of incompletely stabilized nitrocellulose.

Washing.—The nitrocellulose is now submitted to further washing process, after which, if required for specially high-grade lacquers, it may be bleached.

Benzyl Cellulose

The formation of ethers of cellulose is considerably different from that of the esters and the manufacture of benzyl cellulose illustrates these main differences clearly. In this case the first step is to form soda cellulose by the action of caustic soda solution. The strength of this varies with the grade of benzyl cellulose required, but usually it is around 18%. Excess of soda solution is used, and this excess is pressed out before reacting further on the soda cellulose. To the soda cellulose is added benzyl chloride and the mass is

heated for a number of hours, during which the benzylation of the cellulose takes place. The resulting product is benzyl cellulose with by-products such as benzyl alcohol, dibenzyl ether, sodium chloride. These by-products are removed by washing with water and organic liquids. Thereafter the benzyl cellulose is dried. A similar process may be employed in the manufacture of ethyl cellulose.

PLASTICITY OF CELLULOSE ESTERS AND ETHERS

Plastic materials are of high molecular weight and the evidence available shows that they have in common a characteristic chain structure. In plastic materials, such as phenol formaldehyde, the chains are branched. In the earlier part of the paper reference has been made to the structure of cellulose. The main characteristic of this, that is the long chain, is retained by the derivatives of cellulose. It can be accepted that the consequences of almost all physical and chemical treatment of cellulose is to reduce the chain length, and, consequently, even in the most carefully prepared cellulose derivatives, the tensile strength is lower than that of the parent cellulose. In addition, replacement of the hydroxyl group by an ester or ether radicle tends to lessen the cohesional forces and so reduce still further the tensile strength. Another consequence of this is that the effect of temperature is more marked, and is increasingly so as the size of the ester or ether radicle increases.

The effect of the weakening of the cohesional forces on the thermoplasticity of cellulose derivatives is very important. Reference has been made to the absence of softening in cellulose. In contradistinction to this the softening of cellulose derivatives is one of their marked characteristics, and the higher the molecular weight of the ether or ester radicle (in any homologous series) the lower the temperature of softening. Another effect due to weakening of the cohesional forces by the introduction of radicles of high molecular weight instead of the hydroxyl group is to reduce the rigidity of the cellulose fibre and this effect is noticeable when one handles such products as cellulose stearate and cellulose laurate.

Cellulose nitrate, cellulose acetate, cellulose butyrate, and cellulose laurate are plastic materials in the accepted sense in which plastics are referred to in the moulding industry, that is, they soften under heat and pressure, and have a relatively high tensile strength. It is not generally known that nitrocellulose alone, that is without the addition of any other material, is thermoplastic. Indications of its thermoplasticity have been obtained by Dr. Craik of the Nobel Research Laboratories, Ardeer (who has allowed me to refer to this), who has found that nitrocellulose films, when heated at 175—180° C. under oil, lose their shape.

Most other cellulose derivatives are easily recognized as plastics for they can be moulded under heat and pressure without the addition of a second material. It is interesting to note that they soften at lower temperatures as the molecular weights of the esterifying acid increases.

A series of interesting figures dealing with the fatty esters of cellulose are given by Hagedorn and Möller (*Cellulose Chemie*, 1931, pp. 29—33), they give the tensile strengths of films of the fatty esters as decreasing from 9—12 kg. sq. mm. for cellulose acetate down to 0·5 kg./sq. mm. for the stearate, while the % elongation is 15—25 for the acetate and greater than 140 for the stearate. The results agree very well with unpublished work by Dr. Craik. The hygroscopicity of the cellulose fatty esters measured at 72% and 100% saturation also decreases as the molecular weight of the fatty acid radical increases, that of the stearate being approximately 1/10 that of the acetate. The water vapour permeability in these cases is parallel with the hygroscopicity.

From scientific and commercial aspects the plasticizing of cellulose derivatives is of considerable importance; this applies equally to their use in lacquers, films, and moulding powders. The term "plasticizer" is one that is not easy to define and, on the whole, it is safer to use it in the practical sense and not in the scientific sense. We are familiar with the meaning of a solvent, *e.g.*, it is clear what is meant by saying that acetone is a solvent for nitrocellulose. Although it is customary to refer to tricresyl phosphate and castor oil as plasticizers of nitrocellulose the action of each is different.

Tricresyl phosphate is capable of transforming nitrocellulose into a transparent gel, while castor oil alone has no visible effect on nitrocellulose. Nevertheless castor oil is used for maintaining the pliability of films. A useful nomenclature to use in connexion with the above is "gelatinizers" for these substances which convert the cellulose derivatives into gels, and "softeners" for those which do not do this, but nevertheless maintain them in a pliable condition. It has been shown that nitrocellulose adsorbs gelatinizers from non-polar liquids (Desmaroux, *Memorial des Poudres*, 1923, **20**, 71; 1928, **23**, 54), while it shows no affinity for castor oil (a softener) under the same conditions. (Unpublished work by Mr. F. D. Miles and Mr. G. Jones of Nobel Research Laboratories, Ardeer.) The graphical relationship between percentage plasticizer in the non-polar liquid and the quantity of plasticizer adsorbed per gram of nitrocellulose shows the usual type of adsorption curve for compound formation in the case of good plasticizers.

A gelatinizer can be caused to exude from nitrocellulose by the application of pressure, while changes of temperature are sufficient to cause the exudation of a softener. It is possible to obtain an *X*-ray diagram of nitrocellulose containing a plasticizer, which differs from the *X*-ray diagram of its components, but the *X*-ray diagram of nitrocellulose and softener is similar to that of the nitrocellulose alone. The results indicate the formation of a compound between the nitrocellulose and plasticizer. Camphor and most synthetic substitutes for camphor give changes in the *X*-ray diagram, which indicate formation of compounds.

In studying new plastic materials it is useful to obtain preliminary experience by investigating the formation and behaviour of films of the material. The films are prepared from solution, and for ease of handling solvents of suitable volatility are chosen. Thus for nitrocellulose, butyl acetate is satisfactory. The solubility of the cellulose derivative in various liquids is an indication of the type of plasticizer that is effective.

The following is an interesting example of this: It is well known that a mixture of ether and alcohol is a solvent for nitrocellulose. The ethyl ether of ethylene glycol (cellosolve) combines in the same compound the properties of an ether and an alcohol, and thus we have in this product an excellent solvent for nitrocellulose. A high boiling solvent, almost sufficiently high boiling to be put in the gelatinizer class, is the amyl ether of cellosolve. Similarly, cellosolve acetate, like ethyl acetate plus alcohol, is a good solvent for cellulose nitrate, and by analogy we would expect cellosolve stearate to be a good gelatinizer which, in fact, is the case. This principle is also illustrated in the ethers and esters of glycerol.

It will be appreciated therefore that gelatinizers have solvent properties, but differ mainly from the solvents in that their volatility is very low. In general, plasticizers should be non-volatile, good solvents for the cellulose derivative, good solvents for resins, odourless, colourless, and neutral. They should not decompose on storage and should be non-hygroscopic. In addition, plasticizers should be non-inflammable or of low inflammability, and it is desirable, as a rule, that they should impart gloss to the plastic. Films and mouldings which do not contain plasticizers are hard and brittle. Plasticizers should give toughness, whilst all these properties should be permanent.

It would appear to be an advantage that plasticizers should be good solvents for both cellulose derivatives and the resins used in the plastic, since the plasticizer will then help to preserve homogeneity. Further, good solvent power of the plasticizer will tend to prevent its exudation from the film on ageing or on change of temperature. Solid plasticizers are in some cases not satisfactory for there is a tendency for them to crystallize out and this of course causes brittleness. Camphor is exceptional in this respect. Its high volatility makes its use in lacquers unsatisfactory.

Considerable work has lately been carried out in connexion with the testing of elongation and tensile strength of lacquer and enamel films. G. W. Ruudle and W. C. Norris (American Society Testing Materials, 1923) have examined this factor in connexion with the effect of plasticizers on nitrocellulose films. They claim that the retention of distensibility appears to be, within limits, a measure of the life of a film, and that differences between softeners and plasticizers are brought out by stress strain measurements. Using films of equal thickness they measure the elongation produced by different loads.

Examination of the values for volatility and evaporation indicates clearly why dibutyl phthalate has a more permanent effect as a plasticizer than diethyl phthalate although the latter is initially superior, for, after storage for 56 days at 51·7° C., over 60% of the diethyl phthalate has evaporated while only 5% of the dibutyl phthalate has evaporated. Similarly the permanence of the influence of tricresyl phosphate is explained, for it is practically non-volatile at 51·7° C. Diamyl phthalate is reputed to be a superior plasticizer to the dibutyl derivative and it is worthy of notice that the volatility results given above are in agreement with this. The high volatility of camphor accounts readily for its unsuitability in lacquer films.

Mr. F. D. Miles and Mr. G. G. Jones (unpublished work) have made the interesting observation that nitrocellulose film, when absorbing water, increased in tensile strength to a maximum then falling off as the quantity of water increases, while the elongation passes through a minimum. These investigators observed that acetone causes a fall in tensile strength with increase of elongation. Further, in tests on films containing various percentages of dibutyl phthalate they found that the tensile strength was reduced, and that the lower the viscosity of the nitrocellulose with which they worked, then the lower was the tensile strength of the film containing plasticizer. When plasticizer was absent the tensile strength seemed to be independent of the viscosity of the nitrocellulose over a wide range of viscosities. Using tricresyl phosphate as the plasticizer, the effect was to increase the tensile strength to a slight maximum and thereafter a falling off, being parallel with a slight minimum for elongation.

General

The outstanding cellulose plastics are celluloid and certain explosives. Celluloid is a subject which requires special consideration and only brief reference can be made to it here. Considerable inroad has now been made into the trade one time confined to nitrocellulose celluloid by celluloids made from other cellulose derivatives. Celluloids made from cellulose acetate and benzyl cellulose have now become available commercially. These are made by similar processes to that used for making ordinary celluloid. Their main attraction lies in their lower inflammability. As experience is gained in their production, they are likely to replace nitrocellulose celluloid more and more.

A defect of celluloid lies in the time required in the manufacture of the final material, and it is in this connexion that the moulding powders of the newer cellulose derivatives are attractive.

There are two methods in practice for moulding articles from the cellulose derivatives, namely compression moulding and injection moulding.

Compression moulding is carried out in the moulds used for ebonite and bakelite type materials, though much less metal is required. Moulds may be of the "flash" or overflow type, or positive plunger type. The pressure required to make benzyl cellulose compositions flow at their working temperature is a minimum of ½-ton per sq. in. though up to 1 ton is useful and is the usual practice in present-day thermoplastic and thermo-hardening industries. The rate of work with both powder and crêpe form can be improved by pre-heating them. For this, a plate heated with 20—30 lb. steam pressure is used. The crêpe is laid upon the plate, allowed to soften, and folded with beating till the temperature is uniform. It can then be moulded by rapidly pressing in a cold mould, as with bitumen, or in a heated and cooled mould in the case of more complicated or larger articles requiring easier flow.

Injection moulding is usually limited to the production of small shapes or intricate shapes, or mouldings with

difficult inserts. For small articles multiple impression moulds containing perhaps 16 or 20 cavities can be filled in one operation lasting 15 or 20 seconds. The essential part of injection moulding, as practised with thermoplastics of the type of benzyl cellulose and cellulose acetate, is injection into cold moulds. When the material is inside the mould under a pressure on the ram of some 5 to 8 tons per sq. in., and the pressure released, the article can be removed instantly. 3, 4, and 5, or even more injections per minute are thus possible.

The foregoing deals with only a small portion of the amazing story of the developments connected with cellulose plastics. The story of artificial silk is one which has to be omitted from this paper. Hundreds of ingenious minds are working on this and similar problems, and their results are crystallizing at increasing rate in the multitude of patents dealing with cellulose plastics.

From the discussion which followed it was evident that the paper had aroused considerable interest. Mr. Potter asked whether plasticity of cellulose compounds depended on breaking down adhesive force between the molecular chain by chemical action and wished to know what was the true function of a plasticizer.

Dr. Jenkins replied that it appeared that the lateral forces holding the chain-molecules together were cohesional forces and were therefore distinct from the forces holding together the units in the length of the chain molecules which were primary valencies. The functions of a plasticizer were many. Probably the most important was to maintain the homogeneity of the product. In addition it was used to modify the plasticity of the cellulose derivative.

Mr. Sproxton drew attention to the work of Staudinger, which indicated that the chain-lengths were greater than that of 100—200 glucose units put forward by Haworth. It was difficult to believe that Haworth's estimate was large enough. If the viscosity varied as the square of the average chain-length, the latter must vary about thirty-fold, so that if the more viscous cellulose has a chain-length of 200 units, the less viscous would have a chain-length of 6 units, which scarcely seems enough for a nitrocellulose approximating to a lacquer cotton.

Dr. Jenkins said that the average length of chain-molecules in a sample of cellulose was still subject to controversy, but it seemed agreed that the chain-molecules in any fibre were of various lengths. As far as the effects of cohesional forces on thermoplasticity and softening temperature range were concerned, it did not seem that the figure for the average chain-length would alter the point of view.

Dr. Jordan remarked upon the curious parallelism between the viscosity of nitrocellulose and the parent colloid. It seemed difficult to understand how the structure of the parent cellulose could be maintained in the nitrated cellulose in view of the nature of the esterification process. He wished to know whether the lecturer intended to suggest a mechanical interpretation of plasticity. Dr. Jenkins replied that assuming the viscosity of the cellulose and nitrocellulose in their respective solvents depended to some extent on the length of the chain-molecules, the parallelism was not unexpected. In most cases of the nitration of cellulose the reaction was not as vigorous nor as violent as might be anticipated for the fibre structure of the cellulose remained unchanged to a considerable extent in the nitrated cellulose. Bearing this fact in mind, it would be expected that the final molecule chain-length in a nitrocellulose made from cellulose of high viscosity would be greater than from a cellulose of low viscosity.

Major Maclean inquired whether cellulose plastics of higher tensile strength might not be obtained by paying attention to the methods of rolling and extrusion with special reference to the orientation of the chain-molecules. Dr. Jenkins agreed with this view, and pointed out that it seemed likely that the orientation which occurred in the injection process accounted for increased tensile strength as compared with that obtained by the compression process. In reply to a point raised by Mr. C. Chapman, Dr. Jenkins said that plasticizers such as tricresyl phosphate and triphenyl phosphate were very efficient and were still used to a considerable extent for plasticizing nitrocellulose. In reply to a question from Dr. Cutter, Dr. Jenkins said that he was not aware of any successful preparation of mixed ethers and esters of cellulose. Mr. Talbot, Mr. Grant, and Mr. G. Dring also contributed to the discussion, after which the meeting concluded with the chairman's expression of thanks to Dr. Jenkins for his paper.

BRITISH ASSOCIATION OF CHEMISTS

The annual dinner of the London Section was held at the Palace Hotel, Bloomsbury, W.C.2, on Saturday, March 11, at which Mr. H. M. Morgan presided. The attendance was one of the largest ever recorded at the annual dinner, the members and guests numbering 80.

The chairman said that it was interesting to note that the bill now before the House of Lords concerned the question of title, which was a matter in which the Association has been interested for many years.

Dr. E. F. Armstrong proposed "The B.A.C. and London Section." He spoke of the efforts now being made to co-ordinate the work of the societies, and he congratulated the Association upon its willingness to co-operate but also its insistence upon the necessity for autocracy. He thought that co-ordination was a better solution than an attempt to unite. Mr. C. S. Garland replied, and said that the B.A.C. had done a great work for the material interests of the chemist. He congratulated the officers of the Section on their work.

Prof. E. C. C. Baly said that the B.A.C. had a great future, bigger than many people realized. He thought it would ultimately be the controlling factor in the future of chemistry. He thought the *Chemical Practitioner* should be supported by contributions from members.

Mr. S. R. Price proposed "Chemistry and the Guests." He said that it was a great pleasure to welcome the guests who were with them that evening. Some came at inconvenience to themselves which indicated that there was a real link between the Association and those who were interested in it whether they were members or not. With the guests he coupled the name of Dr. Herbert Levinstein. Dr. Levinstein replied, and said it was a great pleasure to accept the Association's

hospitality as a past president. He wished to thank the London Section both on his own behalf and on behalf of the other guests.

Mr. H. E. J. Cory kindly contributed to the musical programme. The dinner was followed by a dance which was greatly appreciated by those present.

CHEMICAL SOCIETY

The first meeting of the Chemical Society under the new scheme for extending the activities of the Society outside London was held in Manchester on Thursday, March 9, in the University Chemistry Lecture Theatre, with Dr. R. H. Pickard, F.R.S., in the chair. Dr. Pickard opened the meeting by explaining briefly the reasons which had led the Council of the Society to depart from its traditional policy of meeting only in London. To give the Fellows increased opportunities to follow and discuss the rapid and far-reaching developments in chemical science which are now taking place, it was felt that meetings in the principal centres outside London had become necessary, and representatives of the Society had been appointed to organize such meetings. The Manchester representatives, Dr. F. Fairbrother and Dr. E. H. Rodd, had been successful in securing Prof. E. K. Rideal, F.R.S. to give the first lecture in Manchester, entitled "How Chemical Reactions 'Go.'"

Starting from the early observed anomalies between collision frequency and rate of reaction in homogeneous systems, the lecturer described the activation hypothesis of Arrhenius and the later work of Bodenstein, Lindemann, and Christiansen, leading to the development of the idea of chain reactions, which was discussed at some length. He then proceeded to discuss modern views on the energy of activation of a chemical reaction and the application of the quantum mechanics to explain how a reaction may come about with less than the normal energy of activation by "tunnelling" through the upper part of a potential energy "hump." A short discussion followed the lecture, in which Mr. M. G. Evans, Dr. H. A. Piggott, and Dr. C. Morson took part. A vote of thanks to Dr. Rideal for his masterly lecture was proposed by Prof. J. Kenner, seconded by Mr. R. H. Clayton and carried with acclamation. The attendance at this meeting numbered over 200, and it is intended during the session 1933—1934 to arrange, in conjunction with other societies in the Manchester district, for other lectures dealing with the mechanism underlying chemical reactions and the contributions which modern chemistry and physics are together making towards their solution.

SOCIETY OF PUBLIC ANALYSTS

The annual general meeting was held at the Chemical Society's Rooms, Burlington House, W., on Wednesday, March 1, when the president, Mr. F. W. F. Arnaud, delivered his presidential address.

The following were elected as Officers and Council for the year 1933: *President:* F. W. F. Arnaud. *Past Presidents serving on the Council:* E. Richards Bolton, J. T. Dunn, Bernard Dyer, Edward Hinks, P. A. Ellis Richards, G. Rudd Thompson, J. Augustus Voelcker. *Vice-Presidents:* John Evans, H. M. Mason, G. W. Monier-Williams, George Stubbs. *Hon. Treasurer:* E. B. Hughes. *Hon. Secretary:* G. Roche Lynch. *Other Members of Council:* H. H. Bagnall, W. T. Burgess, G. D. Elsdon, L. Eynon, C. H. Manley, S. E. Melling, J. R. Nicholls, L. H. Lampitt, H. Lowe, C. E. Sage, J. R. Stubbs, J. F. Tocher.

An ordinary meeting of the Society then followed, the president, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read in favour of:—G. F. Caley, W. R. Dracass, and Y. V. Srikanteswara Iyer.

The following were elected members of the Society: A. T. S. Babb, S. H. Cakebread, H. Phillips, and W. D. Raymond.

CORRESPONDENCE

PHOSPHORIC ANHYDRIDE AS DRYING AGENT

SIR.—On reading a paper on the "Oxidation of Carbonyl Sulphide" by H. W. Thompson, F. L. Hovde and A. C. H. Cairns of the University Museum, Oxford, in pp. 208—216 of the current (February) *Journal of the Chemical Society*, I was amazed to find that not only had the authors of it used unpurified phosphoric anhydride as drying agent for the $COS-O_2$ media, but defended their having done so by adding: "It has been suggested that traces of phosphines thereby introduced vitiate the results. This is very improbable, for the phenomena with COS fall into line with those of CS_2, and if phosphines were present very much lower ignition temps. would be noticed. Moreover, this objection would cast doubt on many of the expts. on reaction kinetics during the past few years."

Fifty years ago two eminent Oxford chemists—H. B. Dixon and H. B. Baker—in their classical researches upon the influence of moisture in combustion demonstrated the *essential* importance of using highly purified gases and the danger of their contamination if and when dried over unpurified phosphoric anhydride. Indeed, we were all taught to regard its special purification before use in such connexion as a most necessary precaution, the non-observation of which would certainly vitiate any and all our experimental results. And from long experience many of us can amply confirm all that was then so wisely insisted on.

Yet, according to this new Oxford style, it would appear that all along we have laboured under a delusion, that we have been wasting our time in unnecessary precautions, and that it matters little whether the phosphoric anhydride used in drying gaseous media be specially purified or not *because*, forsooth, (*inter alia*) if it *did* matter it "would cast doubt on many of the expts. on reaction kinetics during the past few years."

The cat having thus been let out of the bag, is now among the dovecotes with a vengeance. Some of us have felt uneasy about much recent experimental work upon the "kinetics" of so-called "chain-reactions," and here surely is our justification. If, as is now suggested, purification of phosphoric anhydride is merely a fly-blown Victorian superstition, why indeed trouble at all about purifying gases in our researches?

I make bold to say that if, as now seems confessed, much modern work has involved the use of unpurified (*i.e.*, "not specially purified") phosphoric anhydride the results there of are quite unreliable; and in the interests of science I would beg the Chemical Society not to publish more of them unless

assured that the most necessary rule of using carefully purified phosphoric anhydride has been complied with.

I am, Sir, etc.,

WILLIAM A. BONE

London, S.W.
March 10, 1933

PERSONAL AND OTHER ITEMS

Dr J. T. Dunn, of Newcastle, has been nominated as President of the Society for 1933–34.

The Court of London University has appointed Mr James Stinton Jones, M.I.E.E., A.M.I.Mech.E., consultant engineer for heating, lighting, ventilation, and general electrical services in connexion with the new University buildings at Bloomsbury.

Following his resignation from the office of Minister of Transport in the Government, Mr. P. J. Pybus, M.P., has been reappointed a director of the British Portland Cement Manufacturers.

Dr. J. Needham, of Gonville and Caius, Cambridge, has been appointed Sir William Dunn Reader in Biochemistry of the University in succession to Prof. J. B. S. Haldane, who retired from the office recently.

We regret to record the death of Mr. T. H. Appleton who retired a few years ago from the board of directors of H. I. Rowntree & Co., the cocoa and confectionery manufacturers, after having been connected with the firm for nearly 50 years.

We regret to learn of the death on February 3 of M. Paul Bloch, at the age of 83. M. Bloch had taken a prominent part in the development of the chemical industry in France, and was president of the Société des Matières colorantes et Produits Chimiques de Saint-Denis, with whom he had been associated for more than half a century.

Dr. F. C. Wood has withdrawn his acceptance of the post of head of the chemistry department, Hull Municipal Technical College. The post has been filled by the appointment of Mr. L. Balmforth, research chemist of the Imperial Institute, London.

We regret to record the death on March 5 of Mr. William McWhirter, a notable pioneer of the electrical industry. Mr. McWhirter, who was 81 years of age, was responsible for some of the earliest electric lighting installations, including the first dock lighting by arc lamps at Barrow Docks. He was associated with the Faraday Electrical Engineering Works and later founded the firm of William McWhirter & Sons, Ltd., of Glasgow and Cardiff. He was a member of the British Association and had been a member of the Institution of Electrical Engineers since 1880.

Mr. J. W. Wilson, of Leeds, managing director of Wilson & Mathiesons, gas engineers, left estate of the gross value £91,485, with net personalty £89,755.

Chemical Society

In accordance with the general policy of the Chemical Society, the effect of the meeting of Fellows at Sheffield announced in CHEMISTRY AND INDUSTRY of February 24, 1933, is to form a local committee with Prof. G. M. Bennett as chairman and Dr. S. Glasstone as secretary, to arrange meetings and organize other activities of the Society in the Sheffield district.

American Chemical Society

The 86th general meeting of the American Chemical Society is to be held this year on a large scale in Chicago, from September 11 to 15. The meeting coincides with the World's Fair and some of the sessions, including the president's address, will be conducted in the buildings of the Fair, which should add to the attractions of the occasion. A fuller programme will be announced in due course. In the meantime the American Chemical Society issues a cordial invitation to non-American Members of this Society to participate on equal terms with their own members. Mr. Charles Parsons, the secretary, may be addressed at the American Chemical Society, Mills Building, Washington, D.C.

Benefactions to London University

The Armourers and Brasiers' Company and the Carpenters Company have decided to make grants to London University of £2000 and £1000 respectively, in annual payments extending over 10 years. These benefactions, together with £500 granted by the Ironmongers' Company, and £105 by the Dyers' Company will go towards the cost of the ceremonial hall in the new Bloomsbury buildings. The University has also accepted a bequest by the late Mr. Arthur L. Leon of £20,000 for the promotion and encouragement of post-graduate research work.

University College of South Wales

An extension of the Metallurgy Building of the University College of South Wales and Monmouthshire was opened on March 9 by Mr. W. D. Wooley, chairman of the Monmouthshire and South Wales Coalowners' Association. The metallurgical department is stated now to be second only to that at Sheffield.

Metallurgy Lectures

Under the auspices of the Armourers and Brasiers' Company lectures are to be given by Dr. C. H. Desch, F.R.S., on Tuesday and Thursday next, March 21 and 23, at the Royal School of Mines, South Kensington, on "Mosaic Structure in Crystals," and "Crystalline Transformations in Solid Metals." Admission will be free, without ticket.

Diesel-Electric Express Trials

During the holding of the British Industries Fair recently, a Diesel-electric motor-train ran daily to express timings between Euston and Castle Bromwich, Birmingham. Interesting facts regarding its performance have now been made known in a report issued by Sir W. G. Armstrong Whitworth, which states that the cost of the total fuel oil consumed during 2420 miles was only £5 14s., representing a cost per mile of a little more than ½d. Smooth running was maintained at high speeds, whilst the train ran to the express timings without a hitch, in spite of very severe weather conditions.

Plastics Trade Association Meeting

The British Plastic Moulding Trade Association is to be honoured by the presence of H.R.H. Prince George as the guest of honour at its annual luncheon to be held at the Savoy Hotel on Thursday, March 23. Other distinguished visitors will include Sir Harry McGowan, Sir Henry Lyons, the director of the Science Museum at South Kensington, and Prof. G. T. Morgan.

COMPANY NEWS

COURTAULDS, LTD.

In his speech at the 20th ordinary general meeting of Courtaulds, Ltd., on March 9, the chairman, Mr. Samuel Courtauld said that although the company's rayon yarn mills earned a moderate profit in 1932, there was not at present much confidence amongst buyers, and curtailment of production would be necessary if the position did not improve. In America, the year had opened with fairly staple conditions, but consumption became so small that the works of the Viscose Co. were shut down from mid June until the end of July. During August there had come an avalanche of orders, but during the last few weeks it had become plain that the market was again losing its confidence. On the Continent, the course of the rayon industry had been a depressing one, but the trading results of the companies in which Courtaulds held an interest were more favourable than those of their competitors.

There was evidence in America that rayon had lost the stigma which it used to bear as being a mere imitation of a natural fibre, and the same thing was true to a degree in this country and in France. Although rayon had made some progress on account of its low price, it was being pressed very hard by the competition of raw silk. Japanese silk of average quality was last year quoted in America at $1 per lb., which was the lowest in the records for nearly 100 years. Raw cotton was also very low, about 66% below the 1928 level.

Referring to Japanese competition, Mr. Courtauld stated that the policy of undercutting made it difficult to uphold agreements between European producers. The growth of the Japanese industry had been phenomenally rapid. Six years ago her production was only 5,500,000 lb., but in 1932 she was the world's fourth biggest producer, with 68,000,000 lb., and a very small increase would put her above Britain and Italy into second place. The wages of women workers in Japan were about one-eighth of those in England and the Japanese male workers received less for a day's work than was given for an hour's work in England. No general tariff could redress the balance and the position was one which could only be dealt with by exceptional measures.

PINCHIN JOHNSON LTD.

During the year 1932 the number of orders received by the company proved a record in spite of unfavourable conditions. Lower prices resulted however in smaller profit, the net profits for the year being £220,997, a decrease of £51,021 from the amount for 1931. The directors have recommended a final dividend of 7½%, bringing the total for the year to 15%, as against 17½% in 1931. The amount to be carried forward is £47,053, and the special reserve for contingencies has been increased to £43,000.

BRITISH PORTLAND CEMENT MANUFACTURERS

In spite of a reduction in turnover during 1933 trading profits of the company show only a small decrease from the previous year's figure. The total revenue amounted to £731,037, which is a decrease of £7110 compared with 1931. A final dividend of 10% has been recommended on the ordinary shares, bringing the total for the year again to 15%.

MARKET REPORT

This Market Report is compiled from special information received from the manufacturers concerned.

Unless otherwise stated, the prices quoted below cover fair quantities net and naked at sellers' works.

The following alterations in prices are reported since the publication of the last Market Report (cf. **Chem. & Ind.**, Mar. 3, 1933, p. 189).

RUBBER CHEMICALS

Carbon Tetrachloride.—£41—£46 per ton, according to quantity, drums extra.

Diphenylguanidine.—2s. 2d. per lb.

TAR PRODUCTS

Pitch, medium, soft.—90s.—95s. per ton, in bulk at makers' works.

PHARMACEUTICAL AND PHOTOGRAPHIC MATERIALS

Potass. Bitartrate.—99/100% (Cream of Tartar), 82s. per cwt., less 2½%.

ESSENTIAL OILS

Almond.—Foreign S.P.A., 9s. 6d per lb. Anise.—2s. per lb. Bergamot.—7s. per lb. Bourbon Geranium, 24s. 6d per lb.

Camphor.—Brown, 90s. per cwt. White, 90s. per cwt. Cananga, Java, 10s. 9d. per lb. Cinnamon Oil.—4s. 3d. per lb. Cassia, 80/85%, 4s. 9d. per lb.

Citronella Oil.—Java, 2s. 10d. per lb. Ceylon, 2s. 4d per lb. Clove.—90/92%, English, 5s. per lb.

Eucalyptus, Australian B.P., 70/75%.—1s. per lb. Lavender.—Mont Blanc, 38/40%.—11s. per lb. Lemon.—5s. per lb. Lemongrass.—3s. per lb. Orange, Sweet.—6s. 6d. per lb. Otto of Rose.—*Anatolian*, 37s. 6d. per oz.; *Bulgarian*, 55s. per oz. Palma Rosa, 9s. 6d. per lb.

Peppermint.—Japanese, 6s. 9d. per lb. Wayne County, 12s. 9d. per lb. Petitgrain.—6s. 3d. per lb.

GENERAL NOTE

Rapid-filtering Kieselguhr

Kieselguhr has been used for a number of years in operations, such as the production of white sugar, in which special filter-aids are necessary to remove microscopically small particles. Since, however, this material is very variable in quality and may contain impurities affecting its efficiency, efforts have been made during the past few years to improve it, and with very successful results. Rapid-filtering kieselguhr under the tradename of "Filter-guhr" is now sold in an extraordinary high state of purity, being practically insoluble even in acids, and free from organic matter and acid-soluble iron. When this material is deposited on a filter cloth in a thin layer, it becomes possible to remove the finest insoluble matter, and incidentally enables a cloth of cheaper quality to be used in the filter press. The great advantage claimed for "Filter-guhr" is that it increases the rate of flow, whilst giving porous cubes and brilliant filtrates. It is prepared in three grades, No. 70—S a ground powder, No. 701—S an extra-white ground powder, and No. 80—S a white air-floated powder. It is free from acid and in fact slightly alkaline to phenolphthalein, but an absolutely neutral grade can be supplied when required. The manufacturers, the Vereinigte Deutsche Kieselguhrwerke, of Hanover, Germany, are represented in this country by the selling agents, S. Heim, Ltd., Tower House, 40, Trinity Square, London, E.C.3.